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SURVEY REPORTS ON ATMOSPHERIC EMISSIONS FROM THE PHOTOCHEMICAL INDUSTRY

VOLUME IV

AIR PRODUCTS AND CHEMICALS, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

APRIL 1974

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SURVEY REPORTS ON ATMOSPHERIC EMISSIONS FROM THE PETROCHEMICAL INDUSTRY

VOLUME IV

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
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Research Triangle Park, North Carolina 27711

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J. W. Pervier, R. C. Barley, D. E. Field, B. M. Friedman
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This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry. A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in four volumes numbered EPA-450/3-73-005-a, -b, -c, and -d.

This volume covers the following processes: Polypropylene, Polystyrene, Polyvinyl Chloride, Styrene, Styrene-Butadiene Rubber, Vinyl Acetate via Acetylene, Vinyl Acetate via Ethylene, and Vinyl Chloride. For each process the report includes a process description, a process emission inventory, a catalog of emission control equipment, a list of producers, and an evaluation of the significance of the air pollution from the process. Also included is a summary table of emissions to the atmosphere from all the processes studied.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Polyvinyl Chloride	Petrochemical Industry	7A
Carbon Monoxide	Styrene	Particulates	7B
Hydrocarbons	Synthetic Elastomers		7C
Nitrogen Dioxide	Styrene-Butadiene Resin		13B
Sulfur Dioxide	Vinyl Acetate		13H
Polypropylene	Vinyl Chloride		
Polystyrene			

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by

J. W. Pervier, R. C. Barley, D. E. Field,
B. M. Friedman, R. B. Morris, W. A. Schwartz

Houdry Division
Air Products and Chemicals, Inc.
P. O. Box 427
Marcus Hook, Pennsylvania 19061

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry.

A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in these four volumes numbered EPA 450/3-73-005-a, -b, -c, and -d. The Tables of Contents of these reports list the processes that have been surveyed.

Those processes which have a significant impact on air quality are being studied in more detail by EPA. These in-depth studies will be published separately in a series of volumes entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006-a, -b, -c, etc.) At the time of this writing, a total of seven petrochemicals produced by 11 distinctly different processes has been selected for this type of study. Three of these processes, used to produce two chemicals (polyethylene and formaldehyde), were selected because the survey reports indicated further study was warranted. The other five chemicals (carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride and ethylene oxide) were selected on the basis of expert knowledge of the pollution potential of their production processes. One or more volumes in the report series will be devoted to each of these chemicals.

ACKNOWLEDGEMENTS

Survey and study work such as that described in this report have value only to the extent of the value of the input data. Without the fullest cooperation of the companies involved in producing the petrochemicals that have been studied, this report would not have been possible. Air Products wishes to acknowledge this cooperation by commending:

The U. S. Petrochemical Industy
Member Companies of the Industry
The Manufacturing Chemists Association

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IV	Significant Emission Index*
V	Number of New Plants (1973-1980)*

*Fifteen highest ranks from Table I.

NOTE: There are numerous tables and figures in the Survey Reports that are included in the appendicies of this report. These tables and figures are separately listed in each appendix.

SUMMARY

A study of air pollution as caused by the petrochemical industry has been undertaken in order to provide data that the Environmental Protection Agency can use in the fulfillment of their obligations under the terms of the Clean Air Amendments of 1970. The scope of the study includes most petrochemicals which fall into one or more of the classifications of (a) large production, (b) high growth rate, and (c) significant air pollution. The processes for the production of each of these selected chemicals have been studied and the emissions from each tabulated on the basis of data from and Industry Questionnaire. A survey report prepared for each process provides a method for ranking the significance of the air pollution from these processes. In-depth studies on those processes which are considered to be among the more significant polluters either have been or will be provided.

To date, drafts of in-depth studies on seven processes have been submitted. In addition, two further processes have been selected for in-depth study and work on these is in progress. All of these in-depth studies will be separately reported under Report Number EPA-450/3-73-006 a, b, c, etc.

A total of 33 Survey Reports have been completed and are reported here, or in one of the other three volumes of this report series.

I. Introduction

A study has been undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study is to provide data that are necessary to support the Clean Air Ammendments of 1970.

The information sought includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an industry questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

A method for rating the significance of air emissions was established and is used to rank the processes as they are studied. The goal of the ranking technique is to aid in the selection of candidates for in-depth study. These studies go beyond the types of information outlined above and include technical and economic information on "best systems" of emission reduction, the economic impact of these systems, deficiencies in petrochemical pollution control technology and potential research and development programs to overcome these deficiencies. These studies also recommend specific plants for source testing and present suggested checklists for inspectors.

This final report presents a description of the industry surveys that have been completed, as well as a status summary of work on the in-depth studies.

The Appendicies of this report include each of the 33 Survey Reports that were prepared during the course of the study.

II. Discussion

A. Petrochemicals to be Studied

There are more than 200 different petrochemicals in current production in the United States. Many of these are produced by two or more processes that are substantially different both with respect to process techniques and nature of air emissions. Although it may eventually become necessary to study all of these, it is obvious that the immediate need is to study the largest tonnage, fastest growth processes that produce the most pollution.

Recognizing this immediate need, a committee of Air Products' employees and consultants reviewed the entire list of chemicals and prepared a list of thirty chemicals which were recommended for primary consideration in the study and an additional list of fourteen chemicals that should receive secondary consideration. Since this was only a qualitative evaluation it was modified slightly as additional information was received and after consultation with the Environmental Protection Agency (EPA).

The final modified list of chemicals to be studied included all but three from the original primary recommendations. In addition, four chemicals were added and one was broken into two categories (namely low and high density polyethylene) because of distinct differences in the nature of the final products. This resulted in thirty-two chemicals for study and fourty one processes which are sufficiently different to warrant separate consideration. Hence, the following list of petrochemicals is the subject of this study.

Acetaldehyde (2 processes)
Acetic Acid (3 processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (2 processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (2 processes)
Ethylene Oxide (2 processes)
Formaldehyde (2 processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (2 processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (2 processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

B. Preliminary Investigations

Immediately upon completion of the preliminary study lists, a literature review was begun on those chemicals which were considered likely candidates for study. The purpose of the review was to prepare an informal "Process Portfolio" for each chemical. Included in the portfolio are data concerning processes for producing the chemical, estimates of growth in production, estimates of production costs, names, locations and published capacities of producers, approximations of overall plant material balances and any available data on emissions or their control as related to the specific process.

The fundamental purpose of these literature reviews was to obtain background knowledge to supplement what was ultimately to be learned from completed Industry Questionnaires. A second and very important purpose was to determine plant locations and names of companies producing each chemical. This information was then used to contact responsible individuals in each organization (usually by telephone) to obtain the name and address of the person to whom the Industry Questionnaire should be directed. It is believed that this approach greatly expedited the completion of questionnaires. The mailing list that was used is included as Appendix I of this report.

C. Industry Questionnaire

Soon after the initiation of the petrochemical pollution study, a draft questionnaire was submitted by Air Products to the Environmental Protection Agency. It had been decided that completion of this questionnaire by industry would provide much of the information necessary to the performance of the study. The nature and format of each question was reviewed by EPA engineers and discussed with Air Products engineers to arrive at a modified version of the originally proposed questionnaire.

The modified questionnaire was then submitted to and discussed with an Industry Advisory Committee (IAC) to obtain a final version for submission to the Office of Management and Budget (OMB) for final approval, as required prior to any U. S. Government survey of national industries. The following listed organizations, in addition to the EPA and Air Products, were represented at the IAC meeting:

Trade Associations

Industrial Gas Cleaning Institute
Manufacturing Chemists Association

Petrochemical Producers

B. F. Goodrich Chemical Company
E. I. duPont deNemours and Company
Exxon Chemical Company
FMC Corporation
Monsanto Company
Northern Petrochemical Company
Shell Chemical Company
Tenneco Chemicals, Inc.
Union Carbide Corporation

Manufacturers of Pollution Control Devices

John Zink Company
UOP Air Correction Division

State Pollution Control Departments

New Jersey
Texas

The questionnaire, along with a detailed instruction sheet and an example questionnaire (which had been completed by Air Products for a fictitious process that was "invented" for this purpose) were submitted to the OMB for approval. In due course, approval was received and OMB Approval Number 158-S-72019 was assigned to the questionnaire. Copies of the approved instruction sheet, example questionnaire are included as Appendix II of this report.

The questionnaires were mailed in accordance with the mailing list already discussed and with a cover letter that had been prepared and signed by the EPA Project Officer. The cover letter was typed in a manner that permitted the insertion of the name and address of the receipient at the top of the first page and the name of the process, the plant location and an expected return date at the bottom of the first page. A copy of this letter of transmittal is also included in Appendix II.

Understandably, because of the dynamic nature of the petrochemical industry, about 10 percent of the questionnaires were directed to plants which were no longer in operation, were still under construction, were out-of-date processes or were too small to be considered as typical. This did not present a serious problem in most cases because (a) 100 percent of the plants were not surveyed and (b) the project timing permitted a second mailing when necessary. Appendix III tabulates the number of questionnaires incorporated into each study.

One questionnaire problem that has not been resolved is confidentiality. Some respondents omitted information that they consider to be proprietary. Others followed instructions by giving the data but then marked the sheet (or questionnaire) "Confidential". The EPA is presently trying to resolve this problem, but until they do the data will be unavailable for inclusion in any Air Products' reports.

D. Screening Studies

Completed questionnaires were returned by the various respondents to the EPA's Project Officer, Mr. L. B. Evans. After reviewing them for confidentiality, he forwarded the non-confidential data to Air Products. These data form the basis for what has been named a "Survey Report". The purpose of the survey reports being to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". These reports are included as appendicies to this report.

Obviously, significance of pollution [illegible] a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for calculating a Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix IV of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emissions Summary Table that constitutes part of this report. This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes being studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process (Block) flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were established for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) are proposed.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR are proposed.

The bases for these ratings and example calculations are included in Appendix V of this report.

E. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furance Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional processes be "nominated" for in-depth study. The chemicals involved are phthalic anhydride, formaldehyde and ethylene oxide. Work on these indicated a need for four additional in-depth studies as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.
2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst.
3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.
4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

Drafts of these have been submitted to the EPA and reviewed by the Industry Advisory Committee. The phthalic anhydride report also includes a section on production from naphthalene by air oxidation, a process which is considered to be a significant polluter in today's environment but without significant growth potential.

These seven in-depth studies will be separately issued in final report form, under Report Number EPA-450/3-73-006 a, b, c, etc.

An in-depth study, besides containing all the elements of the screening studies, delves into questions such as "What are the best demonstrated systems for emission reduction?", "What is the economic impact of emission control on the industry involved?", "What deficiencies exist in sampling, analytical and control technology for the industry involved?".

In striving to obtain answers to these questions, the reports include data on the cost effectiveness of the various pollution control techniques source testing recommendations, industry growth projections, inspection procedures and checklists, model plant studies of the processes and descriptions of research and development programs that could lead to emission reductions.

Much of the information required to answer these questions came from the completed Industry Questionnaires and the Process Portfolios. However, the depth of understanding that is required in the preparation of such a document can only be obtained through direct contact with the companies that are involved in the operation of the processes being studied. Three methods for making this contact were available to Air Products. The first two are self-evident, as follows: Each questionnaire contains the name, address and telephone number of an individual who can provide additional information. By speaking with him, further insight was obtained into the pollution control problems that are specific to the process being studied; or through him, a visit to an operating plant was sometimes arranged, thus achieving a degree of first hand knowledge.

However, it was felt that these two techniques might fall short of the level of knowledge desired. Thus, a third, and unique procedure was arranged. The Manufacturing Chemists Association (MCA) set up, through its Air Quality Committee (AQC), a Coordinating Technical Group (CTG) for each in-depth process. The role of each CTG was to:

1. Assist in the obtaining of answers to specific questions.
2. Provide a review and commentary (without veto power) on drafts of reports.

The AQC named one committee member to provide liaison. In several cases, he is also one of the industry's specialists for the process in question. If not, one other individual was named to provide CTG leadership. Coordination of CTG activities was provided by Mr. Howard Guest of Union Carbide Corporation who is also on the EPA's Industry Advisory Committee as the MCA Representative. CTG leadership is as follows:

Chemical	AQC Member	Other
Carbon Black	C. B. Beck Cabot Corporation	None
Acrylonitrile	W. R. Chalker Du Pont	R. E. Farrell Sohio
Formaldehyde	W. B. Barton Borden	None
Ethylene Dichloride	W. F. Bixby B. F. Goodrich	None
Phthalic Anhydride	E. P. Wheeler Monsanto	Paul Hodges Monsanto
Ethylene Oxide	H. R. Guest Union Carbide	H. D. Coombs Union Carbide

F. Current Status

Survey Reports on each of the 33 processes that were selected for this type of study have been completed, following review of the drafts by both the EPA and the Petrochemical Industry. These reports constitute the subject matter of this report.

In-depth studies of the seven processes mentioned above have been completed in draft form, submitted to the EPA for initial review, discussed in a public meeting with the Industry Advisory Committee and re-submitted to the EPA in revised form. They are currently receiving final EPA review and will be issued as final reports, following that review.

The EPA has now selected two additional processes for in-depth study and work on these is currently in progress. They are:

1. High Density Polyethylene via the Low and Intermediate Pressure Polymerization of Ethylene.
2. Low Density Polyethylene via the High Pressure Polymerization of Ethylene.

III. Results

The nature of this project is such that it is not possible to report any "results" in accordance with the usual meaning of the word. Obviously, the results are the Survey Reports and In-Depth Studies that have been prepared. However, a tabulation of the emission data collected in the study and summarized in each of these reports will be useful to the EPA in the selection of those processes which will be either studied in-depth at some future date, or selected for the preparation of new source standards. Such a tabulation, entitled "Emissions Summary Table", is attached.

IV. Conclusions

As was stated above under "Results", the conclusions reached are specific to each study and, hence, are given in the individual reports. Ultimately, some conclusions are reachable relative to decisions on processes which require future in-depth studies or processes which warrant the promulgation of new source standards.

A firm basis for selecting these processes is difficult to achieve, but the data contained in the Emissions Summary Table can be of value in setting a basis, or selecting processes.

It is imperative, when using the table, to be aware of the following facts.

1. The data for some processes are based on 100 percent survey of the industry, while others are based on less than 100 percent with some as few as a single questionnaire.
2. Some of the reported data are based on stack sampling, others on continuous monitoring and still others on the "best estimate" by the person responsible for the questionnaire.
3. Air Products attempted to use sound engineering judgement in obtaining emission factors, industry capacities and growth projections. However, other engineering firms, using the same degree of diligence would undoubtedly arrive at somewhat different final values.

Thus, the tabulation should be used as a guide but not as a rigorous comparison of process emissions.

Furthermore, data on toxicity of emissions, odors and persistence of emitted compounds are not included in the tabulation. In addition, great care must be used when evaluating the weighted emission rates because of the wide range in noxiousness of the materials lumped together in the two most heavily weighted categories. For example, "hydrocarbons" includes both ethane and formaldehyde and "particulates" includes both phthalic anhydride and the permanent hardness of incinerated water.

Bearing all of these qualifications in mind, several "top 15" rankings of processes can be made, as in Tables II through V. Obviously, one of these tables could be used to select the more significant polluters directly. Of course, other rankings could be made, such as leading emitters of NO_x or particulates, etc. Using these four tables, however, one analysis might be that the number of times a process appears in these tables is a measure of its pollution significance, or in summary:

Appear in 4 Tables	Appear in 3 Tables
Carbon Black	Acrylonitrile
Low Density Polyethylene	Adiponitrile (Butadiene)
High Density Polyethylene	Ethylene Dichloride (Oxychlorination)
Cyclohexanone	Dimethyl Terephthalate
Polypropylene	Ethylene Dichloride (Direct)
Polyvinyl Chloride	Ethylene
Ethylene Oxide	

Appear in 2 Tables

Maleic Anhydride
Isocyanates
Phenol
Formaldehyde (Silver)

Appear in 1 Table

Phthalic Anhydride
Formaldehyde (Iron Oxide)
Polystyrene
Nylon 6
Nylon 6,6
Vinyl Chloride

Thus, on this basis and in retrospect, it could be concluded that four of the selected in-depth studies (carbon black, ethylene oxide, and both low and high density polyethylene) were justified but that three of them (phthalic anhydride and both formaldehyde processes) were of lesser importance.

On the same basis, seven processes should be considered for future in-depth studies, namely:

Cyclohexanone
Polypropylene
Polyvinyl Chloride
Adiponitrile (Butadiene Process)
Dimethyl Terephthalate (and TPA)
Ethylene Dichloride (Direct)
Ethylene

Obviously, many alternative bases could be established. It is not the function of this report to select a basis for initiating future studies because the priorities of the EPA are unknown. The most apparent of these bases are the ones suggested by Tables II through V, namely the worst total polluters, the worst polluters on a weighted basis, the greatest increase in pollution (total or weighted) or the largest numbers of new plants. In addition, noxiousness of the emissions (photo-chemical reactivity, toxicity, odor, persistence) could be considered in making a selection.

TABLE I
EMISSIONS SUMMARY

Page 1 of 3

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo **Process**	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High **Density** Polyethylene	79	2.3	0	0	0	81.3	6,400
Low **Density** Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) **In most instances** numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low **bias.**
(2) **Assumes** future plants will employ best current control techniques.
(3) **Excludes** methane, includes H_2S and all volatile organics.
(4) **Includes** non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) **Totals** are not equal across and down due to rounding.
(9) **Emissions** based on what is now an **obsolete** catalyst. See Report No. EPA-450/3-73-006-b for up-to-date information.

TABLE I
EMISSION SUMMARY

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	ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) **In most instances** numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) **Assumes** future plants will employ best current control techniques.
(3) **Excludes** methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) **Weighting** factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

TABLE 1
EMISSIONS SUMMARY

Page 3 of 3

	Emissions (2), MM lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	0	1,160	2,460
via Ethanol	27	25	0	966	966
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	56	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	2	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via **Epichlorohydrin**	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,620	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	16.8	650	10	1,523	3,000
Oxo **Process**	6	765	6	[illegible]	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	100	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low **Density** Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	6	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	18	18	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% surveys. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons = 80, particulates = 60, NO_x = 40, SO_x = 20, and CO = 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI"
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut-down of marginal plants.

TABLE II

TOTAL ANNUAL EMISSIONS, ALL "POLLUTANTS", BY 1980 (MM LBS./YR.)*	
Carbon Black	5,730
Acrylonitrile	980
Maleic Anhydride	566
Low Density Polyethylene	343
Cyclohexanone	310
High Density Polyethylene	297
Dimethyl Terephthalate	265
Ethylene Dichloride	253
Phthalic Anhydride (Total)	233
Formaldehyde (Silver)	212
Polypropylene	190
Isocyanates	175
Polyvinyl Chloride	137
Adiponitrile (Butadiene Process)	129
Ethylene Oxide	120

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE III

TOTAL ANNUAL WEIGHTED EMISSIONS BY 1980 (MM LBS./YR.)*	
Acrylonitrile	38,000
Low Density Polyethylene	27,400
Carbon Black	24,740
High Density Polyethylene	23,600
Ethylene Dichloride (Oxychlorination)	16,450
Polypropylene	15,140
Dimethyl Terephthalate	13,500
Cyclohexanone	11,960
Polyvinyl Chloride	10,540
Ethylene Oxide	9,530
Adiponitrile (Butadiene Process)	6,210
Maleic Anhydride	5,670
Ethylene Dichloride (Direct)	5,040
Ethylene	3,670
Phenol	3,640

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE IV

SIGNIFICANT EMISSION INDEX*

Acrylonitrile	23,000
Low Density Polyethylene	21,300
High Density Polyethylene	17,200
Polypropylene	12,190
Ethylene Dichloride (Oxychlorination)	8,800
Carbon Black	7,200
Cyclohexanone	6,260
Dimethyl Terephthalate	6,040
Polyvinyl Chloride	4,840
Adiponitrile (Butadiene)	3,010
Ethylene Dichloride (Direct)	2,740
Maleic Anhydride	2,720
Ethylene Oxide	2,650
Ethylene	2,430
Vinyl Chloride	2,170

*Fifteen higest numbers, as summarized in Table I, for this category.

TABLE V

NUMBER OF NEW PLANTS (1973-1980)*

Low Density Polyethylene	41
Formaldehyde (Silver)	40
Polypropylene	32
High Density Polyethylene	31
Polyvinyl Chloride	25
Polystyrene	23
Ethylene	21
Ethylene Oxide	15
Carbon Black	13
Formaldehyde (Iron Oxide)	12
Phenol	11
Cyclohexanone	10
Isocyanates	10
Nylon 6	10
Nylon 6,6	10
Ethylene Dichloride (Direct)	10

*Fifteen highest numbers, as summarized in Table I, for this category.

Polypropylene

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I. Introduction

Polypropylene has 1) made significant inroads on polyethylene in some product categories such as blow-molded plastic containers, film and sheet, injection molded items, pipe and tubing and coatings; and it has 2) entered in its own right a burgeoning market in polypropylene monofilaments and fibers. In addition, polypropylene is a participant in copolymer materials such as rubber-like elastomers and may have appreciable use in terpolymers; for example, from ternary mixtures like ethylene, propylene and butadiene.

The present polypropylene capacity is predominantly for isotactic homopolymer with copolymer filling out the remainder of the picture. The screening effort in this report is based on questionnaires returned by seven polypropylene manufacturers.

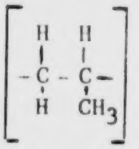
As of mid-1972, approximately 2,050,000,000 lbs./yr. of PP capacity existed in domestic facilities. Emissions arising from these facilities stem primarily from operations concerned with reaction, recovery, drying, purification of materials for recycle, materials handling, storage and packaging; in addition, there is a significant contribution from "fugitive" or "other" emissions. The pollutants are mostly hydrocarbon vapors and polypropylene fines. Relative to pollution significance, PP projections to the year 1980 indicate a weighted SEI of about 12,190 units. This index places polypropylene in the ranks of petrochemicals which may qualify for in-depth studies.

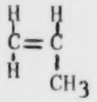
II. Process Description

This is a simplified description of a modern process for the production of isotactic polypropylene.

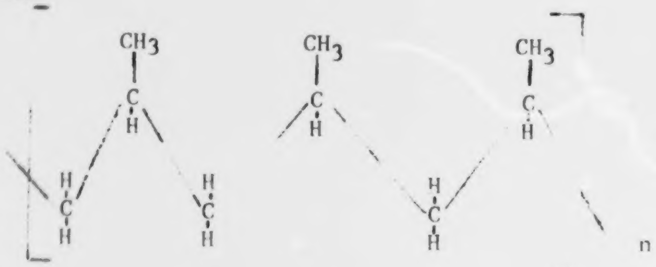
A simplified composite flow diagram is attached. Please see fold-out drawing No. R-212. A Net Material Balance is presented in Table I. Please see Table II relative to a Gross Heat Balance.

Polypropylene resins (PP) are thermoplastics resins containing, predominantly, the following repeating units:

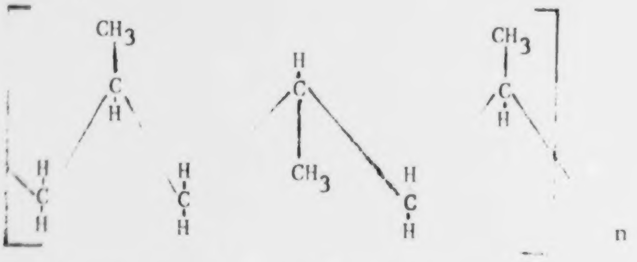

$$\left[-\overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}} - \right]_n$$

The polymerization of propylene,  $\overset{H}{\underset{H}{C}}=\overset{H}{\underset{CH_3}{C}}$, can yield several isomeric polymers, two of which are stereoregular. These are, in simplified form:

(1) Isotactic polypropylene



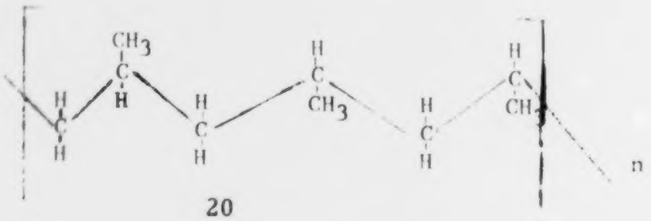
(2) Syndiotactic polypropylene



Both types of stereoregular polypropylene are crystalline and may occur as "left-handed" or "right-handed" helix chains, or as combinations of both.

In addition to these stereoregular polymers, nonstereoregular, atactic polypropylene can be formed:

(3) Atactic polypropylene



Atactic polymers are amorphous and must, in general, be removed from the polymerization product to obtain the desired product specifications, although a small amount is usually required for certain physical properties.

To improve the impact resistance, particularly at low temperatures, propylene is often copolymerized with a small amount of ethylene. Two general types of propylene copolymers are produced: random copolymers and block or impact copolymers. The random copolymers (produced by copolymerizing in a random manner) are more flexible and ductile than homopolymers and are used extensively in film applications. The block or impact copolymers are crystalline copolymers containing alternate segments of polymerized propylene and polymerized ethylene. They exhibit crystallinity normally associated only with stereoregular homopolymers of polypropylene and polyethylene.

Propylene copolymers offer lower brittleness temperatures, higher impact strength and lower notch sensitivity than propylene homopolymers and also offer better moldability, stress crack resistance, stiffness, and tensile strength than polyethylene homopolymers. They are used extensively in molding application where maximum toughness and impact resistance are required.

Polypropylene is produced by heterogeneous polymerization of propylene dissolved in hydrocarbons. Stereospecific catalysts used include systems of the Ziegler-Natta type, e.g., titanium trichloride with aluminum alkyl as co-catalyst, as well as other catalyst systems.*

In most processes used for the manufacture of polypropylene, purified propylene, catalyst slurry and dilution solvent are charged to an agitated reactor. Diluents used include normal and isoparaffins in the C_5-C_8 range, as well as naphthenes such as cyclohexane. However, some processes (e.g., those developed by Eastman Kodak Company, Phillips Petroleum Company and others) do not require a dilution solvent.

During the polymerization reaction, most of the polypropylene formed is precipitated from the solution. The reactor slurry, containing 20-30% solids, is transferred to a flash tank where unreacted propylene and part of the solvent are removed for recycle to the reactor system. The solid material (mostly isotactic polypropylene) and the solvent phase (containing atactic and low-molecular-weight polypropylene) are separated. The isotactic polypropylene can be further purified by reslurrying with a purification solvent and centrifuging, after which it is washed, dried, and stored.

Polypropylene resins and propylene copolymers are produced in many grades and formulations. Molding and extrusion grades are available with low-, medium-, and high-melt flows. Also included are FDA grades, moderate- or high-impact formulations, heat-resistant grades, highly UV-stablilized resins, controlled-crystallinity resins, etc. Controlled crystallinity, obtained by means of nucleating agents, leads to improved clarity and stiffness of the polymer. Resins for the manufacture of films and fibers are also produced in various grades.

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*Because the processes and catalyst systems are similar to those used for high density polyethylene, some plants are equipped to make both products in the same facilities.

Atactic polymer, and some reject polypropylene fines and chunks are buried, incinerated, consigned to landfill, or handled by some other suitable means such as contract disposal.

The PP is extruded and pelletized (or otherwise mechanically prepared) so that it can be fed to the materials handling and finishing system which follows.

The most common form of materials handling system for the pellets is airveying. This type of system permits intermediate and pre-shipment storage in an effectively deployed network of silos.

III. Plant Emissions

A. Continuous Air Emissions

1. Flue Gas

No process fuel usage is reported. Where non-process fuel is used, the amount of fuel and the quantity of sulfur are such that NO_x and SO_2 emissions are negligible.

2. Purification and Recovery Vents

All producers recycle unreacted monomer. The recycle streams require purification. The light and heavy ends from the purification process are either vented, flared, sent to another process or to pollution control. These operations can be one of the sources of air pollution in the production of PP. The reported vent streams in this category, along with their pollution control devices, are summarized in Tables III and IV.

3. Drying and Materials Handling Losses

PP solids are dried, and the semi-finished and finished solids are most often transported in-plant via pneumatic conveying systems. The various atmospheric vents that are associated with these systems are a source of particulate emissions. With suitable retention means such as cyclones and bag filters, continuous particulate emissions are present, but relatively small in amount compared to hydrocarbon vapor emissions. Emission and control device data are summarized in Tables III and IV.

B. Intermittent Air Emissions

1. Routine In-Process Venting

Routine in-process venting is reported by some respondents as a usual occurrence, and present during normal on-stream steady-state operation. One example is in the case of batch operations where each of several reactors goes through a cycle, part of which includes venting. This venting can be directed into a collection system leading to a smokeless flare.

2. Start-Up and Emergency Vents

According to the questionnaire responses received, these vents are normally tied into flare systems. The products of combustion are carbon dioxide and water, except in certain emergencies when the flares receive entrained liquids or excessive gas flows, and may briefly show smoky effluents.

The PP respondents' reports indicate that smokeless flare designs contain adequate safety margin for most situations. However, extreme swings in design parameters occasionally lead to upset conditions; e.g., pilot flame-out; excessive turndown demands; low or zero steam pressure.

NO_x formation resulting from the above start-up and emergency vent flaring is considered inappreciable relative to the national emissions inventory.

C. Waste Water

Water is used (1) is some instances as a polarizing agent to inactivate residual catalyst; (2) to remove residual alcohol from the PP solids when alcohol is employed· (3) in the extrusion steps: (4) as a means of "floating" oily liquids (e.g., in an API pond)· and (5) in some cases as a process vent scrubbing medium, or for direct contact condensation in a steam jet system. Also, waste process water comes from (6) alcohol stripping, where used and (7) amorphous (liquid phase) polymer separation steps where used. The used water is 1) given primary treatment in-house, or 2) is sent off-site for handling by others.

D. Solid Wastes

1. Spent Catalysts

PP catalysts do not pose a solid waste problem. Although the literature indicates numerous variations and nuances relative to PP catalysts, the following explanation represents, in principle, the reason PP catalysts pose no solid waste problem. (Ref.: IEC, 55, No. 2, February, 1963, pages 33, f.)

Polypropylene catalyst material does not dissolve in the diluent or solvent carrier fluid. The catalyst leaves the polymerization area along with the carrier fluid and the insoluble isotactic (product) polypropylene. This catalyst must be deactivated. The deactivation can consist of (1) "dissolving" the catalyst and (2) washing the product polypropylene particles. To prepare for the deactivation procedures, the polymerization area product effluent liquid is sent to a centrifuge or other mechanical separation step. Catalyst contained in the diluent or solvent leaving the mechanical separation step can be deactivated ("dissolved") by polar materials such as alcohols, together with acidifying agents such as hydrochloric acid. The product resin solids retained by the initial mechanical separation step may contain residual undesirable polymeric fractions and a small amount of contaminating catalyst. Organic and water washings to remove this residual material are used to render the isotactic PP fraction suitable for subsequent drying.

The catalyst deactivation and PP product wash streams are directed into further processing steps. They eventually reach a process exit stream such as a distillation (or stripper) column bottoms. The process exit stream becomes part of the waste water. Thus, the catalyst deactivation and removal efforts do not represent a contribution to process waste solids.

2. Polypropylene Waste

The amount of amorphous, non-specification and scrap PP produced (including non-recycled fines) is a function of the process used, the stringency of product molecular weight range specifications, and many other factors. The material is disposed of via incineration, landfill or contract haulage.

3. Miscellaneous

One respondent (25-4) reports "inorganic residue from stripper" under "waste solids", however, the inorganic residue is contained in his "waste water" stream which he says is "treated in our waste treatment facilities". By definition, this "inorganic residue" does not qualify as an entry under "D, Solid Wastes", in this report.

E. Odors

The odors of "propylene" and "paraffinic hydrocarbons" are reported by questionnaire respondents. However, many of the reported vent streams contain materials that have odors. Therefore, it can be assumed that although odors exist they are either undetected or not unpleasant. One respondent (25-6) reports an odor "thought to be primarily hydrogen chloride coming from the polymerization area, and presumed to be from 'weathering of catalyst'".

F. Fugitive Emissions

The respondents indicate fugitive emissions (= "other emissions") of significant proportions, as shown quantitatively in the tabular portions of this report. It is assumed for the purposes of this screening study that all PP operations have significant fugitive emissions; for example, from agitator shaft seals; pump and compressor seals; valve stems.

Liquid storage is 1) padded, 2) pressurized, or 3) low volatility atmospheric tankage. Some alcohol and solvent tanks vent to atmosphere. The respondents are presumed to allot storage losses to "Other Emissions", Section VIII, of the questionnaires, which they, in general, have calculated from their overall material balance.

IV. Emission Control

The various emission control devices that have been reported as being employed by operators of polypropylene plants are summarized in the Catalog of Emission Control Devices, Table IV. In general, no quantitative information on the device performance has been made available. Never-the-less, certain generalizations about the performance of the devices utilized can be made.

Water Scrubbers

A water scrubber device is used by one respondent (25-5) to absorb PP fines and "organometal catalyst" from process vents prior to atmospheric entry.

Cyclones

In polypropylene production, these devices are used to remove or reduce the amount of PP dust emitted from the pneumatic conveyor and silo vent systems. The device efficiencies cannot be calculated from the data reported. But the conclustion may be tentatively drawn that in the future some cyclone installations may be teamed up with or displaced by bag filters.

Bag Filters

For retention of fines, bag filters appear to be the ultimate final-step device for the PP plant of the future. A properly chosen device, according to published literature, will remove substantially all of any PP particulate dust. The bag filters could be used alone, or as back-up for other devices such as cyclones, depending on the specific process requirements.

Flares and Incinerators

All future PP plant operators are presumed to make use of a flare system. Data necessary to calculate combustion efficiencies of existing flares have not been reported. Where specified, flares are mainly associated with the purification and recovery sections. Halogen or sulfur bearing compounds potentially entering the flare systems of the future are not significant relative to the national emissions inventory.

Future operators are presumed to employ incinerators for the (relatively small) combustible liquid waste effluents. Existing incinerators, where reported, appear to make no contribution to the national emissions inventory.

Future operators (and those present operators reporting such devices) are presumed to have flares and incinerators with CCR ratings near 100% and SERR ratings over 99.5%.

The reason for the high presumed CCR rating is that the flares and incinerators of the future (utilizing existing designs) can be of "smokeless" or clear "stack-gas" design with completeness of combustion close to theoretical. Those questionnaire responses reflecting such combustion results (from PP process wastes such as hydrocarbons) show, in general, no indication of incomplete or partial oxidation (for example, no CO).

The above conclusion is based on the definition of "CCR":

$$CCR = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in control device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

The reason for the relatively high presumed SERR ratings is that the highly effective flare and incinerator designs as applied to future PP process pollutant-bearing streams would emit substantially zero particulates and CO, and only the complete-combustion amount of NO_x. There is no pollutant present to form SO_x.

The above conclusion pertaining to the SERR rating is based on the definition of "SERR":

$$SERR = \frac{\text{(weighted pollutants units in)} - \text{(weighted pollutant units out)}}{\text{(weighted pollutant units in)}} \times 100$$

Please see Appendix V of this report for a more detailed explanation. It is demonstrated therein that, for a hydrocarbon pollutant (with complete thermal combustion - as compared to complete catalytic oxidation) the assumption of one pound of nitric oxide formed for each 100 lbs. of HC pollutant, leads to an SERR value of 99.5%. That is

$$SERR = \left(\frac{100 \times 80 - 1 \times 40}{100 \times 80}\right) \times 100 = 99.5\%$$

Compression and/or Cooling or Equivalent

Several respondents (25-1, -2, -3) report as emission control devices systems based on compression and/or cooling to condense and retain components of process vent which would otherwise reach the atmosphere. One respondent (25-3) reports a total net credit of $647,000 per year from such systems.

Screens

Screens with or without felt back-up are reported by one respondent (25-6) to release storage silo conveying air to atmosphere.

V. Significance of Pollution

It is recommended that polypropylene be placed, at present, in a stand-by category relative to the petrochemicals which may qualify for in-depth studies. This recommendation is made because the impact of emissions from new capacity is contingent upon an uncertain projected growth rate: If polypropylene capacity requirements continue to increase at an annual rate closer to the actual figures experienced in recent years (rather than at the lower extrapolated rate of 15% per year used in this report), the production quantity influence (on the SEI)* could be much greater at year 1980. This point is stressed here because published accounts indicate that a few industry observers consider polypropylene to be a "dark horse" compared to polyethylene. That is, polypropylene may not experience as much drop on its future d^2C/dt^2 curve (or rate of decrease in the annual capacity growth rate) as polyethylene has in an equivalent time interval.

A further factor which would couple with the above possibility of high growth rate is the emissions ratio. The emissions ratio for polypropylene is estimated to be 0.032 ton emissions/ton of PP capacity, whereas the emissions ratio for Low Density Polyethylene, for example is about 0.016 T/T LDPE capacity (ref. Survey Report on Low Density Polyethylene see Report No. EPA450/3-73-005c). Thus, for a given installed tonnage of polypropylene capacity, the estimated emissions are about twice the emissions for an equal tonnage of LD polyethylene.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980, and to estimate the total weighted annual emissions from these new plants. This work is summarized in Tables V and VI, respectively.

The Table V forecast of new plants is based on the assumption that the polypropylene growth rate experienced through the year 1972 will project as an annual capacity increase of 15% through 1980. (Reference is made to "Chemical Profile, Polyproplyene, May 22, 1972".) A Significant Emissions Index (SEI) of 12,190 has been calculated. See Table VII. Of this total, 12,160 units stem from hydrocarbon vapors, equivalent to increased emissions (by 1980) of 152,000,000 lbs./year.

If polypropylene qualifies later for an in-depth study, a further point appears to warrant consideration: The respondents "in toto" cover a wide spectrum with respect to assignment of emissions to 1) fugitive sources, and 2) all other sources. Almost all of the reported emissions (to atmosphere) may be shown under "Fugitive" or "Other" labelling in one instance, whereas "Fugitive Emissions" may appear to account for only a small portion of the total in another instance. As a constituent of an in-depth study, it would seem that further definition and resolution of this picture is required.

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*See Appendix IV for definition.

VI. Polypropylene Producers

The following tabulation of polypropylene producers indicates published production capacity:

Company	Location	Capacity MM Lbs./Yr. Estimated as of August, 1969*
Amoco Chemicals	New Castle, Del.	200
Dart Industries	Odessa, Texas	50
Diamond Shamrock	Deer Park, Texas	70
Eastman Kodak	Longview, Texas	90
Enjay Chemical	Baytown, Texas	150
Hercules, Inc.	Lake Charles, La. Parlin, N. J.	370
Novamont Corp.	Neal, W. Va.	80
Shell Chemical Co.	Woodbury, N. J	150
	Total	1,160

*For the 3rd quarter of 1972, the estimated total capacity is 2,050 MM lbs./yr., based on figures submitted by questionnaire respondents and published projections.

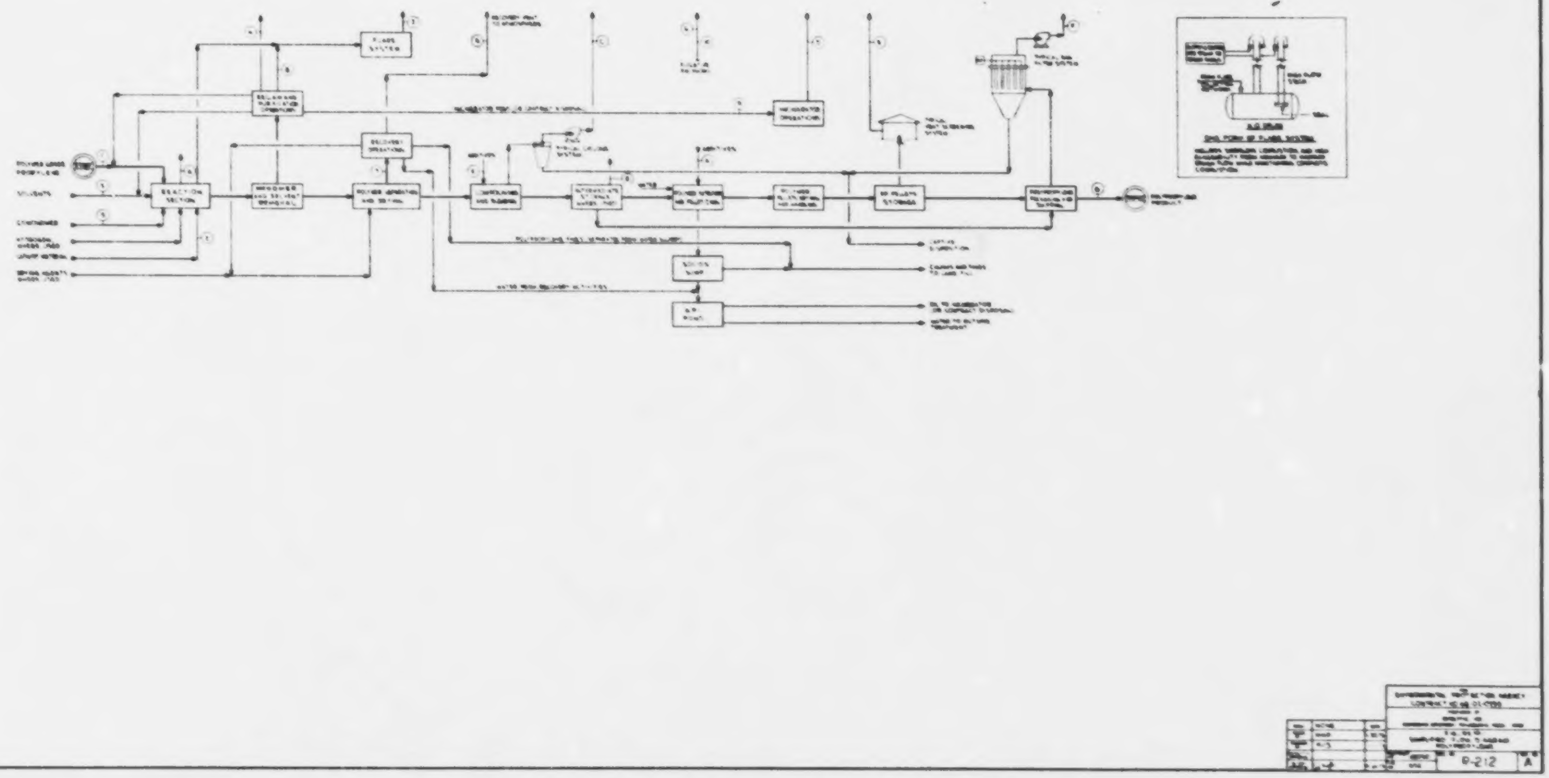
REACTION SECTION
SOLVENTS
COMONOMER
FLARE SYSTEM
RECOVERY OPERATION
WATER
POLYPROPYLENE PRODUCT
K.O. DRUM
ONE FORM OF FLARE SYSTEM
P-212
A

TABLE PP-I
COMPOSITE POLYPROPYLENE
NET MATERIAL BALANCE
(TONS/TON OF PP CAPACITY)

		Stream No. on Simplified Flow Diagram	Polymer Ingredients	Other
INPUT				
Polymer grade propylene		1	1.0800	
Catalyst		2		0.00613
Solvents		3		0.01077
Antioxidants, stabilizers, additives		4	0.0062	
Polymer grade ethylene (comonomer)		5	0.0035	
Total Input			1.0897	0.01690
OUTPUT				
Crystalline PP and copolymer		6	1.0000	
Polymer separation, drying	PP fines	7	0.0057	
	Propylene		0.0084	
Reclaim	Propylene	8	0.0020	
Residue from reclaim operations	Propylene	9	0.0101	
	Propane		0.0019	
	Catalyst			0.0021
	Solvents			0.0074
Semi-liquid amorphous	Propylene		0.0319	
Fugitive emissions (monomer leaks)		10	0.0200	
Total Output*			1.0800	0.0095

*Exclusive of losses from storage tanks.

TABLE PP-II
POLYPROPYLENE
GROSS HEAT BALANCE

The exothermic heat of propylene homopolymerization is order-of-magnitude 960 BTU/Lb. (1)

---

(1) The equivalent figure for polyethylene is reported as 1,450 BTU/lb. in "Chem. Eng.", 73 (16) 68-August 1, 1966. As a crude approximation, the propylene value, assuming equal monomeric molar heats of homopolymerization, is 1,450 times (28.05)/(42.08) or 966.6, which is rounded down to 960 BTU/lb. A log-log plot for heats of homopolymerization for ethylene, 1,3-butadiene and styrene indicates, by interpolation, a value of approximately 840 for polypropylene.

TABLE PP-III
NATIONAL EMISSIONS INVENTORY
POLYPROPYLENE

Page 1 of 4

Company							
Location							
EPA Code No.	25-1			25-2	25-3	25-4	
Capacity - Tons of Polypropylene/Yr.	60,000			150,000	62,500	75,000	
Average Production - Tons of PP/Yr.	60,000			150,000	62,500	75,000	
Seasonal Range in Production - % of Max.	0			0	0	0	
Emissions to Atmosphere							
Stream - Letter on Flow Diagram	H_1	H_2	G	B	G	B	G
Description	Reclaim Vent	Purification Vent	Fugative	Recovery Vent	Fugative	Recovery Vent	Fugative
Flow - Lb./Hr. of Pollutants	344	54	Not quantified	729	303	15	Not quantified
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous		Continuous	Continuous	Continuous	
if Intermittent - Hrs./Yr. Flow							
Composition - Ton/Ton of PP							
Hydrocarbons	0.0229	0.0036		0.0212	0.0194	0.0008	
Particulates							
NO_x							
Sample Location					"Discharge Opening"		
Date or Frequency of Sampling	Not sampled	Not sampled		Not sampled	Once	Not sampled	
Type of Analysis					Chromatograph		
Odor Present	None	None		Yes	None	Not indicated	
Vent Stacks	Yes	Yes		Not indicated	Yes	Yes	
Flow - SCFM per stack	120	9			91 total	754	
Number	1	1			20	1	
Height - Feet	35	75			16	42	
Diameter - Inches	1½	2			4	8	
Exit Gas Temperature - °F	Ambient	60° F			150 max	212	
Emission Control Device	Yes	No			Yes	No	
Type - Flare							
Bag Filters							
Cyclone							
Water Scrubber							
Other	Condenser			Condenser	Condenser		
Catalog I. D. Number	25 - 1.102			25 - 2.103	25 - 3.104		
Total Hydrocarbon Emissions - Ton/Ton PP	0.0229	0.0036		0.0212	0.0194	0.0008	
Total Particulate - Aerosol Emissions - Ton/Ton PP	None	None		None	None	None	
Total NO_x - Ton/Ton PP	None	None		None	None	None	
Total SO_x - Ton/Ton PP	None	None		None	None	None	
Total CO - Ton/Ton PP	None	None		None	None	None	

TABLE PP-III
NATIONAL EMISSIONS INVENTORY
POLYPROPYLENE

Page 2 of 4

Company				
Location				
EPA Code No.	25-5			
Capacity - Tons of Polypropylene/Yr	50,000			
Average Production - Tons of PP/Yr	50,000			
Seasonal Range in Production - % of Max	0			
Emissions to Atmosphere				
Stream - Letter on Flow Diagram		B	D	G
Description		Scrubber Vent	Incinerator Stack	Fugitive
Flow - Lb./Hr. of Pollutants		25.3	23	238
Flow Characteristic - Continuous or Intermittent		Continuous	Continuous	Continuous
If Intermittent - Hrs./Yr. Flow				
Composition - Ton/Ton of PP				
Hydrocarbons		0.0085		0.0200
Particulates			0.0018	
NO_x			0.0001	
Sample Location				
Date or Frequency of Sampling		Not sampled	Not sampled	
Type of Analysis				
Odor Present		None	None	
Vent Stacks		Yes	Yes	
Flow - SCFM per stack		21	5,900	
Number		4	1	
Height - Feet		90	20	
Diameter - Inches		4	84	
Exit Gas Temperature - F°		130	1,800	
Emission Control Device		Yes		
Type - Flare				
Bag Filters				
Cyclone				
Water Scrubber				
Other		Scrubber	Incinerator	
Catalog I. D. Number		25 - 5.101, - 102, - 103, - 104	25 - 5.105	
Total Hydrocarbon Emissions - Ton/Ton PP		0.0085		0.0200
Total Particulate - Aerosol Emissions - Ton/Ton PP		None	0.0018	
Total NO_x - Ton/Ton PP		None	0.0001	
Total SO_x - Ton/Ton PP		None	None	
Total CO - Ton/Ton PP		None	None	

TABLE PP-III
NATIONAL EMISSIONS INVENTORY
POLYPROPYLENE

Company						
Location						
EPA Code No.				25-6		
Capacity - Tons of Polypropylene/Yr				140,000		
Average Production - Tons of PP/Yr				140,000		
Seasonal Range in Production - % of Max				0		
Emissions to Atmosphere						
Stream - Letter on Flow Diagram	A	F	B	C	E & I	G
Description	Reaction Vent	Comp. Seal Leakage	Recovery Vent	Compounding	Handling & Storage	Fugative
Flow - Lb./Hr. of Pollutants	12 Average	32	200	400	3.9 Total	Not quantified
Flow Characteristic - Continuous or Intermittent	Intermittent	Continuous	Continuous	Continuous	Continuous	
if Intermittent - Hrs./Yr. Flow	Not indicated					
Composition - Ton/Ton of PP						
Hydrocarbons	0.0003	0.0008	0.0053	0.0105	0.0001 Total	
Particulates	0.0001*					
NO_x						
Sample Location		Roof-top vent	Not indicated	"Sample Taps"		
Date or Frequency of Sampling	Not Sampled	Once per year	Once per year	on-line analyzer	Not Sampled	
Type of Analysis		Chromatograph	Chromatograph	Chromatograph		
Odor Present	Yes (HCl)	Yes (HC)	None	None	None	
Vent Stacks	Yes	Yes	Yes	Yes		
			F-1 F-2 F-3		I I-1 I-2 N-1 N-2 N-3	P-1 P-2
Flow - SCFM per stack		16	3 47 10	400	10M 3M Total 22M Total	16 M Total
Number	1	1	1 1 1	1	1 1 1 1 1 1	1 1
Height - Feet	26	25	18 34 35	50	35 85 85 85 85 85	40 15
Diameter - Inches	8	1½	1½ 20 1½	6	20 x 22 12 29 x 29 12 29 x 29 53 x 41	13 x 13 10
Exit Gas Temperature - F°	Ambient	75 - 150	60-90 90-110 60-90	100	120 120 120 ·110 110 110	110 140
Emission Control Device	No	No	No No No	No	Yes Yes Yes Yes Yes Yes	Yes Yes
Type - **Flare**						
Bag Filters						X X
Cyclone					X	
Water						
Other					25-6 Screens Screens	
Catalog I. D. Number					102 25-6.103 25-6.104	25-6.105
Total Hydrocarbon **Emissions** - Ton/Ton PP	0.0003	0.0008	0.0053	0.0105	None	
Total Particulate - Aerosol **Emissions** - Ton/Ton PP	0.0001	None	None	None	0.0001 Total	
Total NO_x - Ton/Ton PP	None	None	None	None	None	
Total SO_x - Ton/Ton PP	None	None	None	None	None	
Total CO - Ton/Ton PP	None	None	None	None	None	

*Average figure resulting from estimation (based by respondent on material balance) of HCl from "decomposition of catalyst"

TABLE PP-III
NATIONAL EMISSIONS INVENTORY
POLYPROPYLENE

Page 4 of 4

Company					
Location					
EPA Code No.			25-7		
Capacity - Tons of Polypropylene/Yr			300,000		
Average Production - Tons of PP/Yr			262,500		
Seasonal Range in Production - % of Max			0		
Emissions to Atmosphere					
Stream - Letter on Flow Diagram	A	H	B	H	H
Description	Reaction Vent	Purification Vent	Drying Vent	Recovery Vent	Recovery Vent
Flow - Lb./Hr. of Pollutants	440	1,525	310	665	30
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
If Intermittent - Hrs./Yr. Flow					
Composition - Ton/Ton of PP					
Hydrocarbons	0.0064	0.0222	0.0045	0.0097	0.0004
Particulates					
NO_x					
Sample Location	Discharge lines		Dryer influent		
Date or Frequency of Sampling	Once per year	Not sampled	3 times per day	Not sampled	Not sampled
Type of Analysis	Chromatograph		Steam dist.		
Odor Present	No	No	No		No
Vent Stacks	Yes	Yes	Yes	Yes	
Flow - SCFM per stack	0 - 100	1,200 Total	1,200 - 20M total	2,400 Total	"Unknown"
Number	28	25	8 dryers	16	3
Height - Feet	75 - 100	100	85 - 100	40	100
Diameter - Inches	2 - 3	2 - 4	8 - 36	2 - 4	6
Exit Gas Temperature - F°	100 - 130	90 - 160	185 - 220	220	185
Emission Control Device	None	None	Yes	None	None
Type - Flare					
Bag Filter					
Cyclone			X		
Water					
Other					
Catalog I. D. Number			Not numbered		
Total Hydrocarbon Emissions - Ton/Ton PP	0.0064	0.0222	0.0045	0.0097	0.0004
Total Particulate - Aerosol Emissions - Ton/Ton PP	None	None	None	None	None
Total NO_x - Ton/Ton PP	None	None	None	None	None
Total SO_x - Ton/Ton PP	None	None	None	None	None
Total CO - Ton/Ton PP	None	None	None	None	None

TABLE PP-IV
CATALOG OF EMISSION CONTROL DEVICES
POLYPROPYLENE

Page 1 of 3

FLARE SYSTEM			
Device I. D. Number*	25-1.101	25-3.101	25-4.101
Types of Compounds Flared	Various HC's	Various HC's	Various HC's
Amount Flared - lb./hr	40M** (Normally near zero)	Variable	3,336 calc'd. average
Device or Stack Height - ft	112	Flare pit	200
Stack Diameter @ Tip - inches	18		24
Installed Cost - Mat'l. & Labor - $	96,416	78,000	299,000
Installed Cost - Mat'l. & Labor - $/lb. of PP Production	0.0803	0.0624	0.1993
Operating Cost - Annual - $ (1972)	6,089	14,100	102,500 Credit***
Operating Cost - Annual $/lb. of PP Production	0.0051	0.0113	0.0683 Credit
Efficiency - CCR - %	Presumed near 100%	Presumed near 100%	Presumed near 100%
Efficiency - SEKR - %	Presumed over 99.5%	Presumed over 99.5%	Presumed over 99.5%
Years Installed	1961	1972	1971
Source	John Zink Co.	In-house	John Zink & Wyatt Div (U. S. Industries, Inc.)

MISCELLANEOUS			
Device I. D. Number*	25-1.102	25-2.100	25-2.101
Purpose - Control Emission of	Process Vapors	Process Vapors	PP Fines
Type	Compression and Cooling	B. D. Drum & water spray	Bag Filters - 27 total
Rate	Variable	Emergency	Not indicated
Installed Cost - Mat'l. & Labor, $	46,815	75,000	189,000
Installed Cost - Mat'l. & Labor, $/lb. of PP Production	0.0390	0.0250	0.0630
Operating Cost - Annual - $ (1972)	12,660	2,000	57,000
Operating Cost - $/lb. of PP Production	0.0106	0.0007	0.0190
Efficiency	Not indicated	Not indicated	Not indicated
Years Installed	32.4M 1963, 4.2M 1966, 10.2M 1967	1971	1969, 1970
Sources	In-house	In-house	Yound Mach.

*EPA code number for questionnaire respondent followed by emission control device number used by the respondent.

**Design rate.

***For 25-4.101, credit is taken for "spent hexane" liquid recycle from flare K. O. drum.

TABLE PP-IV
CATALOG OF EMISSION CONTROL DEVICES
POLYPROPYLENE

Page 2 of 3

FLARE SYSTEM		
Device I. D. Number*	25-5.106	25-6.101
Types of Compounds Flared	Various HC's	Various HC's
Amount Flared - lb./hr.	20,000** (Norm. 40)	5,996 calc'd. average
Device or Stack Height - Ft.	138	250 above grade
Stack Diameter @ tip - Inches	20	8" for the above rate
Installed Cost - Mat'l. & Labor - $	37,000	78,000
Installed Cost - Mat'l. & Labor - ¢/lb. of PP Production	0.0370	0.0278
Operating Cost - Annual - $ (1972)	14,000	108,000
Operating Cost - Annual - ¢/lb. of PP Production	0.0140	0.0386
Efficiency - CCR- %	Presumed near 100%	Presumed near 100%
Efficiency - SERR - %	Presumed over 99.5%	Presumed over 99.5%
Years Installed	35M 1963, 2M 1972	28M 1962, 2M 1968, 10M 1971, 38M 1972
Source	John Zink Co.	John Zink flare tips

MISCELLANEOUS					
Device I. D. Number*	25-2.102	25-2.103	25-3.102	25-3.103	25-3.104
Purpose - Control Emission of	Liquid to Atmos.	Process vapors	PP Fines	Process vapors	Process vapors
Type	K. O. Drum	Condenser and K. O. Drum	Bag Filters; 5 total	Condenser and K. O. Drum	Condenser
Rate	Not indicated	Not indicated	143 lbs./hr	1,585 lbs./hr.	8 lbs./hr
Installed Cost - Mat'l. & Labor, $	100,000	10,000	68,600	20,300	3,850
Installed Cost - Mat'l. & Labor, ¢/lb. of PP Production	0.0333	0.0033	0.0549	0.0162	0.0031
Operating Cost - Annual - $ (1972)	2,000	2,000	2,100	640,200 Credit	6,780 Credit
Operating Cost - ¢/lb. of PP Production	0.0007	0.0007	0.0017	0.5122 Credit	0.0054 Credit
Efficiency	Not indicated	Not indicated	Not indicated	Not indicated	Variable
Years Installed	1970	1970	21.3M 1963, 14.0M 1965, 33.3M 1970	1970	1.7M 1963, 2.1M 1970
Sources	In-house	Not indicated	Flex Kleen Co	Not indicated	Not indicated

*EPA code number for questionnaire respondent followed by emission control device number used by the respondent.
**Design rate.

TABLE PP-IV
CATALOG OF EMISSION CONTROL DEVICES
POLYPROPYLENE

Page 3 of 3

MISCELLANEOUS				
Device I. D. Number*	25-5.101, 5.102, 5.103, 5.104	25-5.105	25-6.105-1,-2	25-6.102
Purpose - Control Emission of	Process Vapors	Process Fluids	PP Fines	PP Fines
Type	Scrubber	Incinerator**	Bag Filters	Cyclones
	4 total			
Rate	68 lbs./hr.	Variable	180 lbs./hr.	Variable
Installed Cost - Mat'l. & Labor, $	6,000	41,600	102,500	7,700
Installed Cost - Mat'l. & Labor, ¢/lb. of PP Production	0.0060	0.0416	0.0366	0.0028
Operating Cost - Annual - $ (1972)	20,800	37,200	750 Credit	5,600
Operating Cost - ¢/lb. of PP Production	0.0208	0.0372	0.0003 Credit	0.0020
Efficiency	98.5	99.5+ on HC's	99.3	Not indicated
Years Installed	1971	33.6M 1963, 7.5M 1971, 0.5M 1972	52.9M 1961, 31.5M 1964, 18.1M 71	6.5M 1971, 1.2M 1972
Sources	In-house	Thermal Research & Eng'g. Co.	Dracco Co. & Flotronics Co.	F. B. Witte Co.

MISCELLANEOUS			
Device I. D. Number*	25-6.103-1,-2	25-6.104-1,-2,-3	25-7
Purpose - Control Emissions of	PP Fines	PP Fines	"Emission Control devices such as dryer cyclones, vent condensers and gas neutralizers are considered integral parts of the process and are not shown separately"
Type	Screens	Screens	
Rate	Variable	Variable	
Installed Cost - Mat'l. & Labor, $	5,200	23,700	
Installed Cost - Mat'l. & Labor, ¢/lb. of PP Production	0.0019	0.0085	
Operating Cost - Annual - $ (1972)	100	500	
Operating Cost - ¢/lb. of PP Production	0.00004	0.0002	
Efficiency	Not indicated	Not indicated	
Years Installed	3.6M 1961, 0.8M 1969, 0.8M 1971	14.2M 1961, 5.3M 1964, 1.6M 1967, 1.8M 1969, 0.8M 1971	
Sources	Metal Arts, Inc.; Dracco Co.	Metal Arts, Inc.; Dracco Co.	

*EPA code number for questionnaire respondent followed by emission control device number used by the respondent

**Item 25-5.105 is included by the respondents as an emission control device.

TABLE PP-V
NUMBER OF NEW POLYPROPYLENE PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be added by 1980	Economic Plant Size	Number of New Units
1,160	120 Estimated	1,040	5,040 Estimated	5,800*	4,760	150 Estimated	32

All rates are in MM lbs./yr.

*Basis 2,050 MM lbs./yr. capacity for mid-1972 with ensuing projected growth rate of 15% per year through 1980.

TABLE PP-VI
EMISSION SOURCE SUMMARY
TON/TON OF POLYPROPYLENE

Emissions	Source					Total
	Reaction Area	HC Recycle	Recovery Area	Materials Handling	Fugitive Emissions	
Hydrocarbons	0.0003	0.0008	0.0053	0.0105	0.0150*	0.0319
Particulates	0.0001	None	None	None	None	0.0001
NO_x	None					0.00
SO_x						0.00
CO						0.00

*Assumed to be a true fugitive figure for a new, "clean", well-maintained installation.

TABLE PP-VII
WEIGHTED EMISSION RATES

Chemical Polypropylene

Process Various; e.g., Ziegler-Natta and Bulk Slurry Polymerization

New Added Capacity by 1980 4,760 MM LBS./YR.

Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factor	Weighted Emissions Units
Hydrocarbons	0.0319	152	80	12,160
Particulates	0.0001	0.5	60	30
NO_x	Negligible		40	0
SO_x	None		20	0
CO	None		1	0

Significant Emissions Index = 12,190

Polystyrene

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I. Introduction

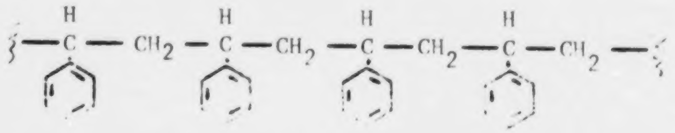
The postwar (WW II) development of the polystyrene industry in the U. S. is due, in no small part, to the extensive efforts of the CPI to develop and produce synthetic rubber (GR-S) for the war effort. Less than 1 million pounds of styrene based plastic was produced in 1937, today, over 2,500 million pounds are produced annually. About twenty years ago, when the 100 million pounds/year mark was achieved, general purpose styrene accounted for the bulk of the production. Today, rubber-modified polymers (high impact polystyrene, etc.) are, at least, of equal importance. The low cost, ease of fabrication, and ease of modification are all responsible for the dramatic growth of this industry.

The prime air pollutant associated with the production of polystyrene is styrene. It is emitted during feed preparation (if any), from the reaction section and from the devolatilization process. Additionally, polystyrene dust is discharged to the atmosphere by the pneumatic conveying systems generally used. Also, varying quantities of waste water are produced. In general, however, the production of polystyrene generates relatively little air pollution.

The current U. S. polystyrene production capacity is approximately 3.5×10^9 lbs./yr. This includes general purpose polystyrene, high impact polystyrene and various co-polymers, but excludes SBR rubber and S/B latex. Production capacity will nearly double by 1980, increasing to 6.7×10^9 lbs./yr.

II. Process Description

Styrene polymerizes quite readily with the addition of either heat or an initiator (catalyst), such as benzoyl peroxide or ditertiary butylperbenzoate. Styrene will homopolymerize in the presence of diverse inert materials and copolymerize with a variety of monomers. Pure polystyrene has the following structure:



Although polymers with molecular weights in the millions can be made, those most useful for molding have mol. wts. of about 125,000, while those used in the surface coating industry average about 35,000.

Several techniques are empolved to polymerize styrene. In order of decreasing commercial importance they are: (1) solution polymerization, (2) suspension polymerization and (3) emulsion polymerization. The first two are the most important, and the subject of this report, as shown (Fig. FS -1).

Solution Polymerization

A mixture of styrene and solvent (such as ethylbenzene) is fed into a series of tubular, agitated polymerization reactors. The reactors are normally constructed of aluminum or stainless steel. Each reactor contains several heat exchange zones to remove the large heat of reaction generated during the polymerization. The mixture flows from top to bottom of each reactor, entering the first reactor at about 250° F and leaving the last reactor at about 340° F. The solvent maintains the viscosity of the polymerizing mass within manageable limits and facilitates heat removal.

The solvent containing polymer is pumped from the last reactor into a low pressure high temperature devolatilizer, where unreacted monomer and solvent are flashed off. These vapors are condensed and recycled to monomer feed. The polymer (polystyrene) is extruded, cooled, cut and conveyed to product storage.

Suspension Polymerization

In suspension polymerization, small droplets of styrene (0.1 to 1 MM) are dispersed in water. The polymerization is carried out batchwise in stirred, jacketed reactors. Polymer is produced in the form of small beads or pearls. The water, at a water/monomer ratio of from 1 to 3, acts as a heat transfer agent and keeps the monomer/polymer droplets at a uniform temperature. The result is a product more uniform than from any other (styrene polymerization) process. Generally, reaction initiators and suspending agents are required.

The water/polymer bead mixture is pumped from the reactor to a wash tank, where the suspending agents and initiators are removed. However, polymer contamination by residual amounts of these materials normally results and polymer purity is lower than for other processes.

The washed beads are separated from the wash water by centrifuge, after which they are dried and extruded. At this stage the polymer is treated as it is in the solution process.

III. Plant Emissions

A. Continuous Air Emissions

1. Feed Preparation Section Purge

Only one respondent (EPA Code No. 26-4) has reported an emission from this source. Said respondent is the sole reporting employer of the solution polymerization process, which reputedly is quite sensitive to catalyst poisons...i.e. feed contaminants. The natural inference is that this type emission is to be expected of plants utilizing solution polymerization whereas it is atypical of the suspension process plants. The actual emissions reported are summarized in Table III.

2. Reactor Vent

Respondent 26-1, having observed reactor liquid level decrement during reaction, has calculated and reported the corresponding emissions. They amount to over 700,000 lbs./yr. of styrene and 300,000 lbs./yr. of water. Other operators have reported neither emissions from this source, nor devices to prevent them. However, respondents 26-2 and 26-3 offer no quantitative data on polluting emissions from any source, so lack of supportive information should not deter one from surmising that reactor vapors are normally vented to the atmosphere, and that they represent a significant portion of the total emissions for the process.

3. Solvent Recovery Section Vent

As would be expected, only the solution polymerization plant (EPA Code No. 26-4) has reported emissions from this source. For this plant those emissions constitute the single largest source of atmospheric pollution, contributing nearly 75% of the total hydrocarbons emitted. On a lb./lb. basis they equal .00184 lbs. of hydrocarbon (styrene) per pound of polystyrene.

4. Polymer Drying Vents

Both plants 26-2 and 26-3 report emissions from streams in this category. With one minor exception, the contaminants in these streams are only identified, with no information given on their concentration. In general, these vents are air streams containing small amounts of polystyrene (plant 26-3) or pentane and hydrochloric acid (plant 26-2). Other available information is summarized in Table III.

5. Pneumatic Conveyor Exhaust

After polymerization, polystyrene undergoes a number of finishing operations - extrusion, pelleting, coloring, packaging, etc. The requisite polystyrene transportation is provided by a system of pneumatic conveyors. There are always a number of conveyor exhaust streams (vents) associated with such a system. The components of the vents are normally air and polymer dust, occasionally the vent will contain some water (vapor) or traces of volatile hydrocarbons. The respondents have provided no quantitative emission data on these streams.

6. Extruder Exhaust

Respondents 26-2 and 26-3 both report emissions from this source. Again, no quantitative data is available, but apparently the exhaust air contains small amounts of styrene.

B. Intermittent Air Emissions

1. Emergency Vents - Reactor Section

Only respondent 26-3 mentions emissions in this category. It seems reasonable to assume that other plants encounter emergencies similar to those described by 26-3 - "depending on the emergency, emissions could range from steam vented for pressure reduction to styrene monomer vapor released from emptying the entire contents of a reactor containing semi-polymerized styrene. Emergencies such as power failure or loss of suspension may necessitate emptying the entire contents of a reactor".

2. Feed Preparation Purge

Respondent 26-4 reports a small styrene vent (<.00001 lbs./lb.) arising from the cyclic filling and venting of a feed prep. tank. As discussed in Section III-A-1, no other respondents have feed prep. sections.

C. Continuous Liquid Wastes

The only liquid waste reported was waste water. However, there was considerable variation in the quantities reported:

Plant	Quantity Gal./Hr.	Contaminants	Treatment
26-1	8,333	Not Specified	Aeration - Clarification
26-2	58,200	Not Specified	Yes
26-3	1,240	Not Specified	Yes
26-4	120 to 180	Et. Bz & Styrene	No

D. Intermittent Liquid Wastes

None reported.

E. Solid Wastes

All respondents report the disposal of solid wastes, specifically, scrap polystyrene or waste 'resin'.

Operator 26-1 reports 2 x 10^6 lbs./yr. waste polystyrene - all of which is disposed of in sanitary land fills.

Operator 26-2 reports disposing of 26,000 lbs./day of waste resin. Half is taken directly to land fill areas and half is discharged into settling ponds from waste water streams.

Operator 26-3 reports only 100 lb./day of waste polystyrene. This is disposed of by the municipal waste department.

F. Odors

In general, the production of polystyrene does not appear to have an associated odor problem.

The respondents reported no odor complaints in the past year. All of the reported odors are said to be detectable only on the plant property and only at intermittent intervals. The material causing odors in this category has been identified as styrene. However, according to the questionnaires, these emissions are well enough controlled to prevent odor problems.

G. Fugitive Emissions

Fugitive emissions for the subject process appear to be negligible. Operator 26-2 summarizes the reasons: "Process is basically a low pressure/atmospheric operation predominantly handling solids --- (Hydrocarbon) ---- piping is minimal and pumps are equipped with mechanical seals. Leakage is nil".

H. Other Emissions

Two operators (26-3 and 26-4) report using a sulfur containing fuel. SO_x emissions on a lb./lb. basis are .00033 and $<.00001$ respectively. No other sources of significant emissions have been reported.

IV. Emission Control

The few emission control devices that were reported as being employed by respondents to the questionnaire pertaining to the subject process, are summarily described in Table IV of this report. An efficiency has been assigned each device when data sufficient to calculate it have been available. Three types of efficiency are normally calculated:

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{lbs. of specific pollutants in} - \text{lbs. of specific pollutant out}}{\text{lbs. of specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR}^* = \frac{\Sigma(\text{lbs. of pollutant} \times \text{wf}) \text{ in} - \Sigma(\text{lbs. of pollutant} \times \text{wf}) \text{ out}}{\Sigma(\text{lbs. of pollutant} \times \text{wf}) \text{ in}} \times 100$$

*where wf = weighting factor designated in Table VII of this report.

Usually a combustion type control device (i.e. incinerator, flare etc.) will be assigned both a "CCR" and a "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V of this report.

Cyclones

Only one operator (EPA Code No. 26-3) reports the use of cyclones for emission control. In this instance he utilized them (3) to recover polyethylene particles from the dryer exhaust stream. The particles range in size from 2.5 to 60 microns with the majority 20 μ. The cyclones are designed to remove 96% of the 16+ μ material. However, it would seem that this particular installation might better be characterized as a product recovery system, rather than a pollution control system, for its total installed cost is $1625 whereas it recovers $998,750 worth of polystyrene annually! Aside from the design number (96%) given above, no data were presented which would indicate its actual efficiency.

Bag Filters

Only one operator (EPA Code No. 26-3) reports the use of bag filters to control emissions. The filters are used to separate polystyrene particles from the (exhaust) air used to convey them. The respondent provided no data from which actual collection efficiencies could be calculated. However, if one assumes that the particle size distribution is similar to that given above, then collection efficiencies of 99 + % are to be expected.

Based on the gross economics presented in Table IV, Catalog of Emission Control Devices, it would seem that these filters (PS-2 and PS-3) would be better characterized as product recovery devices. It seems reasonable to assume that most polystyrene producers utilize them, and no other respondent listed them as emission control devices.

Based on the questionnaire responses, it would seem that the polystyrene industry employs few (if any) air pollution control devices. Thus, although atmospheric emissions are apparently not high, the utilization of existing technology could undoubtedly significantly decrease air emissions associated with the production of polystyrene.

Development work is not required to reduce emissions. The employment of currently available devices would be effective in significantly reducing emissions from the subject process.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. The reported emission data indicate that the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed. However, the presented appraisal of the quantity of polluting emissions is subject to error from more sources than usual. They are:

A. The data from two processes (suspension and solution) have been integrated and presented as a whole.

B. There is no quantitative data to support the estimate of particulate emissions, they could be considerably higher.

C. The difference between 1980 capacity and demand (see Table V) is quite large. If this is unrealistic (and the 1980 capacity should be closer to demand) then the SEI* would be appreciably lower.

Never-the-less, because A and B (above) tend to be self-compensating and because the SEI* is quite low, it is believed that the characterization of the process as a relatively low air polluter is accurate.

The methods outlined in Appendix IV of this report have been used to estimate the total weighted emissions from new plants. This work is summarized in Tables V, VI and VII.

Published support for the Table V forecast of new plants may be found in Appendix C of Process Research's final report on Task Order No. 14 for the EPA (August 13, 1971).

On a weighted emission basis a Significant Emission Index of 1,641 has been calculated in Table VII. This is substantially less than the SEI's that are anticipated for some of the other processes in the study. Hence, the recommendation to exclude polystyrene from the in-depth study portion of the overall scope of work.

---

*Significant Emission Index - see Appendix IV.

VI. Polystyrene Producers**

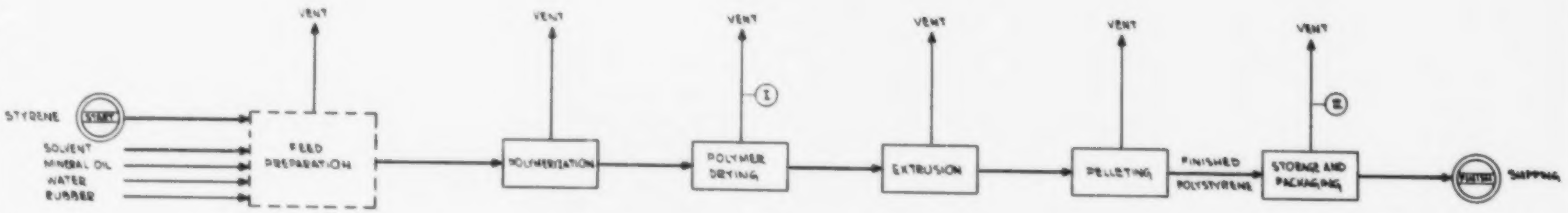
The following tabulation of polystyrene producers indicates published production capacity by company and plant location:

Plant	Location	Capacity - MM Lbs./Yr.
Alabama Binder & Chem. Co.	Tuscaloosa, Ala.	
American Petrofina	Big Spring Texas	150
	Calumet City, Ill.	150
BASF	Jamesburg N. J.	80
Beatrice Foods	Wilmington, Mass.	
Borden	Illiopolis, Ill.	
	Bainbridge, N. Y.	
	Compton, Calif.	
	Demopolis. Ala.	
	Leominster Mass.	
Dart Industries	Holyoke, Mass.	50
	Joliet, Ill.	40
	Ludlow, Mass.	30
	Santa Ana, Calif.	20
Diamond Plastics	Long Beach Calif.	60
Dow	Gales Ferry, Conn.	150
	Ironton, Ohio	270
	Midland, Mich.	250
	Riverside, Mo.	10
	Torrance. Calif.	130
Foster Grant	Leominster, Mass.	120
	Peru, Ill.	80
Gorden Chem.	Oxford, Mass.	30
	Worcester, Mass.	50
Howard Industries	Hicksville, N. Y.	
S. C. Johnson & Son	Racine, Wisc.	
Monsanto	Addyston, Ohio	375
	Long Beach, Calif.	375
	Springfield, Mass.	375
Morton Chem.	Ringwood. Ill.	
O'Brien Co.	South Bend, Ind.	
Fuller - O'Brien Co.	South San Francisco Calif.	
Pennsylvania Indust. Chem.	Clairton, Pa.	
Philip Morris	Springfield, Conn.	
Polymeric Resins	Wilmington, Mass	
Polysar	Leominster, Mass.	60
Purex	Bristol, Pa.	
	Carson, Calif.	
	Chicago Ill.	
Reichhold	Elizabeth, N. J.	
Richardson Co.	West Haven, Conn.	50
Scholler Bros.	Elwood, N. J.	
Shell	Belpre, Ohio	60
Sinclair Koppers	Kobuta, Pa.	300
Southern Petrochemicals	Channelview, Texas	60
Staley Chem.	Kearney, N. J.	
	Lemont, Ill.	
	Marlboro Mass.	
Standard Oil of Indiana	Joliet, Ill.	70
	Medina, Ohio	25
	Torrance, Calif.	25
	Willow Spring, Ill	50
	Leominster, Mass.	20

Plant	Location		Capacity - MM Lbs./Yr.
Sybron Corporation	Haledon, N. J.		
Union Carbide	Bound Brook, N. J		65
	Marietta, Ohio		100
U. S. Steel	Haver Hill, Ohio		200
		Total*	3,130

*Of known capacities, 1971.

**Straight and rubber modified, may include certain styrene co-polymer resins and elastomers.


STYRENE
START
SOLVENT
MINERAL OIL
WATER
RUBBER
FEED PREPARATION
VENT
POLYMERIZATION
VENT
POLYMER DRYING
I
VENT
EXTRUSION
VENT
PELLETING
VENT
FINISHED POLYSTYRENE
STORAGE AND PACKAGING
II
VENT
FINISH
SHIPPING

NOTE

ROMAN NUMERALS (I) ARE CROSS-REFERENCE IDENTITIES FOR CATALOG OF EMISSION CONTROL DEVICES - TABLE II

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. 19102

FIGURE PS-1
BLOCK FLOW DIAGRAM
POLYSTYRENE PRODUCTION

SCALE	NONE	DATE
DRAWN BY	HHP	2-27-75
CHECKED BY	RBM	3-10-75
CATALYTIC APPROVAL		
CLIENT APPROVAL	DWP	7-8-75

PROJECT NO. 42090	DWG. NO.	REV. NO.
L.O. NO. 436	R-219	A

TABLE PS-I
POLYSTYRENE PRODUCTION

MATERIAL BALANCE - T/T OF POLYSTYRENE

There are not sufficient published data available to permit the presentation of a meaningful material balance.

TABLE PS-II
POLYSTYRENE PRODUCTION

GROSS REACTOR HEAT BALANCE

The exothermic heat of polystyrene homopolymerization is 290 BTU/Lb. of monomer.

There are not sufficient published data available to permit the construction of a typical commercial reactor section gross heat balance for this process.

TABLE PS-III
NATIONAL EMISSIONS INVENTORY
POLYSTYRENE PRODUCTION
VIA
'SUSPENSION' AND 'SOLUTION' PROCESSES

Page 1 of 3

Plant EPA Code No.	26-1	26-2					
Capacity, Tons of Polystyrene/Yr.	100,000	150,000					
Range in Production - % of Max.	None	None					
Emissions to Atmosphere Stream	Reactor Vent	Washing Exhaust (A)	Dryer Exhausts (B)	Blender/Check Bin Purge Exhausts (C)	"Airveying" Systems Exhaust (D)	Extruder Exhausts (E)	Airveying Systems Exhaust (Extruder Area)
Flow - Lbs./Hr.	1,140,000/Yr	137,520	261,288	229,200	105,432	91,680	32,088 (F)
Flow Characteristic, Continuous Or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
If Intermittent, Hrs./Yr. Flow							
Composition, Tons/Ton of Polystyrene							
Styrene	.00399					+	
Polystyrene					+		
Water	.00171						
Pentene		+	.00002	+	+		
Nitrogen							
Ethyl Benzene							
Hydrochloric Acid		+					
Air		4.04471	7.68494	6.74117	3.10094	2.69647	
Vent Stacks	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Number	1	10	6	17	20	2	7
Height - Ft.	4	40 to 50	20 to 50	20 to 80	10 to 80	10	10 to 60
Diameter - Inches	2	12 to 18	12 to 48	5 to 18	5 to 8	12 x 12	5 to 8
Exit Gas Temp. - F°	195 - 270	Ambient	Ambient to 120°	Ambient	Ambient	Ambient	Ambient
SCFM/Stack	1500	3000 (Avg.)	6330 (Avg.)	2940 (Avg.)	1150 (Avg.)	10,000	1000 Avg.
Emission Control Devices	None	None	Yes	None	Yes	Yes	Yes
Cyclone Separator			+				+
Bag Filter					+		+
Condenser/K. O. Drum							
Other						H.E. Scrubber	
Analysis							
Date or Frequency of Sampling	Never	Never	One time	Never	Never	Never	Never
Sample Tap Location	N/A	N/A	Not Specified	N/A	N/A	N/A	N/A
Type of Analysis	Calc'd.	Calc'd.	Calc'd.	Calc'd.	Calc'd	Calc'd	Calc'd.
Odor Problem							
Summary of Air Pollutants							
Hydrocarbons, Ton/Ton of Polystyrene	.00399						
Particulates, Ton/Ton of Polystyrene	0						
NO_x, Ton/Ton of Polystyrene	0						
SO_x, Ton/Ton of Polystyrene	0						
CO, Ton/Ton of Polystyrene	0						

+) Rate cannot be determined.
+)

TABLE PS-III
NATIONAL EMISSIONS INVENTORY
POLYSTYRENE PRODUCTION
VIA
'SUSPENSION' AND 'SOLUTION' PROCESSES

Page 2 of 3

Plant EPA Code No	26-3						
Capacity, Tons of Polystyrene/Yr	58,750						
Range in Production - % of Max	None						
Emissions to Atmosphere							
Stream	Emergency Vents - Reactor Section	Dryer Exhaust Vent (G)	Pneumatic Conveyor Vent (H)	Pneumatic Conveyor Vent (M)	Extruder Hood Exhaust Vent	Pneumatic Conveyor Vent (H)	Pneumatic Conveyor Vent
Flow - Lbs./Hr	Not Specified	39,652	20,324	6,231	14,898	5,603	5,603
Flow Characteristic, Continuous or Intermittent	Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
If Intermittent, Hrs./Yr. Flow	Not Specified						
Composition, Tons/Ton of Polystyrene							
Styrene	+				+		
Polystyrene		+	+	+		+	+
Water	+				+		
Pentane							
Nitrogen							
Ethyl Benzene							
Hydrochloric Acid							
Air		2.95621	1.51528 (Avg.)	.46455 (Avg.)	1.11071	.41778 (Avg.)	.41778 (Avg.)
Vent Stacks	No	Yes	No	No	Yes	No	No
Number		3			1		
Height - Ft.		41 │ 31 │ 26			60		
Diameter - Inches		15 │ 16 x 20 │ 3 x 8.5			27		
Exit Gas Temp. - F°		160 │ 150 │ 150			180		
SCFM/Stack		2570 │ 4340 │ 1740			3310		
Emission Control Devices	None	PS-1	PS-2	PS-2	None	PS-3	PS-3
Cyclone Separator		+					
Bag Filter			+	+		+	+
Condenser/K. O. Drum							
Other							
Analysis	None		None	None	None	None	None
Date or Frequency of Sampling	Never	One time	Never	Never	Never	Never	Never
Sample Tap Location	N/A		N/A	N/A	N/A	N/A	N/A
Type of Analysis	N/A	Std. Seive	N/A	N/A	N/A	N/A	N/A
Odor Problem	No	No	No	No	No	No	No
Summary of Air Pollutants							
Hydrocarbons, Ton/Ton of Polystyrene	Cannot be determined.						
Particulates, Ton/Ton of Polystyrene							
NO_x, Ton/Ton of Polystyrene							
SO_x, Ton/Ton of Polystyrene							
CO, Ton/Ton of Polystyrene							

TABLE PS-III
NATIONAL EMISSIONS INVENTORY
POLYSTYRENE PRODUCTION
VIA
'SUSPENSION' AND 'SOLTUION' PROCESSES

Plant EPA Code No.	26-4						
Capacity, Tons of Polystyrene/Yr.	10,000						
Range in Production - % of Max.	None						
Emissions to Atmosphere							
Stream	Feed Prep. Purge	Feed Prep. Purge	Solvent Recov. Section Vent	Hood Exhaust From Extrusion & Pelleting Sections	Pelletizer Vent	Hood Exhaust From Extrusion + Pelleting Sections	Pneumatic Conveyor Purge
Flow - Lbs./Hr.	24	4	80	6,876	4,497	6,876	4,813
Flow Characteristic, Continuous or Intermittent	Continuous	Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent, Hrs./Yr. Flow		3 Hrs./Day					
Composition, Tons/Ton of Polystyrene							
Styrene	.00032	<.00001	.00077				
Polystyrene				+		+	+
Water					.05602		
Pentane							
Nitrogen	.00871	.00022	.02945				
Ethyl Benzene	.00033	<.00001	.00107				
Hydrochloric Acid							
Air				2.70709	1.71449	2.70709	1.89496
Vent Stacks	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Number	1	1	1	1	1	1	4
Height - Ft.	35	50	45	25	25	25	30 to 60
Diameter - Inches	8 x 24	12	1	7 x 8	10 x 12	7 x 8	3 to 10
Exit Gas Temp. - F°	Ambient	Ambient	85	90	90	90	100°
SCFM/Stack	5	1	17	1500	1000	1500	1050
Emission Control Devices	No	No	No	No	No	No	No
Cyclone Separator							
Bag Filter							
Condenser/K. O. Drum							
Other							
Analysis							
Date or Frequency of Sampling	Never	Never	Never	Never	Never	Never	Never
Sample Tap Loaction	None	None	None	None	None	None	None
Type of Analysis	Calc'd.	Calc'd	Calc'd.	Calc'd.	Calc'd.	Calc'd.	Calc'd.
Odor Problem	No	No	No	No	No	No	No
Summary of Air Pollutants							
Hydrocarbons, Ton/Ton of Polystyrene	.00249						
Particulates, Ton/Ton of Polystyrene	+						
NO_x, Ton/Ton of Polystyrene	0						
SO_x, Ton/Ton of Polystyrene	0						
CO, Ton/Ton of Polystyrene	0						

TABLE PS-III
NATIONAL EMISSIONS INVENTORY
POLYSTYRENE PRODUCTION
VIA
SUSPENSION AND SOLUTION PROCESSES

EXPLANATION OF NOTES

(A) Ten separate streams comprise this entry, some are continuous and some are intermittent. Flow rates and pollutant concentrations are based on the average total flow.

(B) The exhausts from six driers comprise this entry. Flow rates and pollutant concentrations are based on the average total flow.

(C) The discharges from seventeen blender/check bin purge 'exhausters' comprise this entry. Flow rates and pollutant concentrations are based on the average total flow.

(D) The exhausts from twenty 'airveying' systems comprise this entry, some are continuous and some are intermittent. Flow rates and pollutant concentrations are based on the average total flow.

(E) The discharges from two rotoclones comprise this entry. Flow rates and pollutant concentrations are based on the combined flow.

(F) The exhausts from seven 'airveying' systems comprise this entry, some are continuous and some are intermittent. Flow rates and pollutant concentrations are based on the average total flow.

(G) The exhausts from three driers comprise this entry. Flow rates and pollutant concentrations are based on the combined flow.

(H) The exhausts from three pneumatic transfer systems comprise this entry. Conveyor operation is intermittent, but flow rates and pollutant concentrations are based on total flow, averaged over twenty-four hour period.

TABLE PS-IV
CATALOG OF EMISSION CONTROL DEVICES
POLYSTYRENE PRODUCTION
VIA
SUSPENSION & SOLUTION PROCESSES

	Solvent Removal Section		Extrusion Section	Packaging & Product Storage
CYCLONES				
EPA Code No. for plant using	26-3			
Flow Diagram (Fig. II) Stream I.D.	I			
Device I. D. No.	PS-1 (A)			
Control Emission of	Polymer Dust			
T-T Height - Ft.				
Diameter - Ft.				
No. of Stages				
Installed Cost - Mat'l. & Labor - $	1,625			
Installed Cost based on - "year" - dollars	1958 to 1970			
Installed Cost, c/lb. of Polystyrene/Yr.	.00138			
Operating Cost, Annual - $ (1972)	140			
Value of Recovered Product, $/Yr.	998,750			
Net Operating Cost, $/Yr.	-998,610			
Net Operating Cost, c/lb. of Polystyrene	(Negative)			
Efficiency - SE - %	96 (of 16 u part.)			
Efficiency - SERR - %				
BAG FILTERS				
EPA Code No. for plant using		26-3		26-3
Flow Diagram (Fig. II) Stream I. D.		I		II
Device I. D. No.		PS-2 (B)		PS-3 (C)
Control Emission of		Polymer Dust		Polymer Dust
Number of Compartments				
Number of Bags/Compartment				
Total Bag Area - FT^2				
Bag Cloth Material				
Design (operating) temp. - F^o		(130)		(130)
Design (operating) press - PSIG				
Installed Cost - Mat'l. & Labor - $		37,000		2,600
Installed Cost Based on - "year" - dollars		1958 to 1969		1958 to 1962
Installed Cost, c/lb. of Polystyrene/Yr.		.03149		.00221
Operating Cost - Annual - $ (1972)		18,580		260
Value of Recovered Product - $/Yr.		149,800		20,000
Net Operating Cost - $/Yr.		-131,220		-19,740
Net Operating Cost - c/lb. of Polystyrene		(Negative)		(Negative)
Efficiency - SE - %				
Efficiency - SERR - %				

TABLE PS-IV
CATALOG OF EMISSION CONTROL DEVICES
POLYSTYRENE PRODUCTION
VIA
SUSPENSION & SOLUTION PROCESSES

EXPLANATION OF NOTES

(A) Three similar cyclones comprise device PH-1. Costs detailed in Table IV are total costs.

(B) Twenty-four "flo-tronics bin vent filter assemblies" comprise device PS-2. Costs detailed in Table IV are total costs for all 24 assemblies.

(C) Seven filter units comprise device PS-3. Costs detailed in Table IV are total costs.

TABLE PS-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980*	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
3,500	225	3,275	5,500	6,700	3,425	150	22 - 23

Note: All capacities in MM Lbs./Yr.

*1980 demand based on process research report.

TABLE PS-VI
EMISSION SOURCE SUMMARY
TON/TON OF POLYSTYRENE

	Source						
Type	Feed Preparation Section	Reactor Vent	Solvent Recovery Section	Conveying Operations	Fired Heater Flue Gas	Fugitive Emissions	Total
Hydrocarbon	.00065	.00334	.00184				.00583
Particulate				.00010			.00010
NO_x						Negligible	0
SO_x					.00033		.00033
CO							0

TABLE PS-VII
WEIGHTED EMISSION RATES

Chemical Polystyrene

Process Homopolymerization

Increased Capacity by 1980 3,425 MM Lbs./Yr.

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factor	Weighted Emissions MM Lbs./Yr.
Hydrocarbons	.00583	19.97	80	1597.6
Particulates	.00010	.34	60	20.6
NO_x	0	0	40	0
SO_x	.00033	1.13	20	22.6
CO	0	0	1	0

Significant Emission Index = 1640.8

Polyvinyl Chloride

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Emission Source Summary	Table PV-VI
Weighted Emission Rates	Table PV-VII

I. Introduction

The term "polyvinyl chloride (PVC) resins" is meant to include vinyl chloride homopolymers with the repeating unit $-CH_2CHCl-$ and copolymers of vinyl chloride with minor amounts of vinyl acetate, ethylene, propylene, vinylidene chloride or acrylates. Most are available in the form of white powders that, after compounding with a number of auxiliary ingredients, are converted into a large variety of plastic or resinous end products through several types of processes. Because PVC resins are thermoplastic, all but one of these processes for converting PVC powders employ heat to make the end product (coating resins are processed by dissolving the resin and applying it from solution).

Industrial development of PVC resins began some 40 years ago. Production on a full commercial scale began in Germany in 1931 and in the United States in the later 1930s, after the discovery that polyvinyl chloride, when heated in the presence of a suitable high-boiling liquid (a plasticizer), formed a flexible plastic material that resembled rubber or leather. Because plasticized PVC showed itself to be a good insulator, resistant to the weather, and nonflammable, it was put to military uses in World War II. Diversified compounding and processing technology, which developed particularly in the later 1940s and early 1950s, quickly led to many broad-scale commercial uses.

The processing and performance characteristics of PVC resins can be varied with the molecular weight, which for most commercial PVC resins lies between 50,000 and 120,000. Equally important to the characteristics of the resins is the presence or absence of plasticizer. Most PVC plastics produced in past decades were flexible types, containing plasticizer. While the many processes for plasticized PVC are relatively easy to carry out, the processing of PVC compounds containing essentially no plasticizer (for the production of rigid PVC plastics) is technically more demanding. The properties of plasticized PVC plastics depend greatly on the exact amounts and chemical types of plasticizers used; it is common to employ mixtures to achieve the desired properties.

Although the great majority of PVC resins used in the various processes to manufacture PVC plastics are homopolymers of vinyl chloride, copolymers are still essential in some processes, where they are used alone or in admixture with homopolymers.

The most important commercial copolymers of vinyl chloride are those with vinyl acetate. The higher molecular weight resins with an acetate content of about 2-8% are used for calendering and extrusion, where somewhat faster processing is possible because of their better flow properties compared with those of conventional homopolymers. Copolymers containing over 8% vinyl acetate flow even more readily under the application of heat and pressure and are, therefore, favored in the production of phonograph records. The copolymers also are capable of binding particularly large amounts of mineral fillers and pigments, a capability utilized in the production of vinyl-asbestos floor tile. Because the solubility in esters and ketones of vinyl chloride copolymers with an acetate content of 10-20% is much greater than that of homopolymers, these resins are used in solution coating.

The commercial copolymers of vinyl chloride with ethylene and propylene contain 1-8% of ethylene or propylene and are predominantly used in the manufacturing of unplasticized (rigid) PVC products. Such copolymers can be processed faster and have better impact strenght than comparable homopolymers, without any sacrifice in dimensional stability and other important performance properties.

Copolymers of vinyl chloride with vinylidene chloride are more soluble in solvents than homopolymers and they are good film formers. The few resins of this type that are on the market today are, therefore, mostly used in specialty coatings (in solution and, in some applications, in latex or emulsion form).

A few latex PVCs or copolymers of vinyl chloride and ethyl, n-butyl, or 2-ethylhexyl acrylate are used in the production of wall coverings, nonwovens, and house paint. The latexes are 50 percent solid colloidal dispersions in water.

Postchlorinated PVC homopolymer resins have long been in existence but were of little commercial importance until recently. Products made from them have better heat resistance (and higher densities) than products made from ordinary PVC resins. The main application for these resins is in residential hot water pipe.

The present polyvinyl chloride capacity is mainly for various structural forms of the homopolymer (see under "Process Description"), with copolymer filling out the remainder of the picture. The survey activity represented in this report is based on questionnaires returned by seven polyvinyl chloride manufacturers.

As of February, 1972, approximately 4,375,000,000 lbs./year of PVC capacity existed in domestic facilities. Emissions arising from these facilities stem primarily from operations concerned with monomer storage; reaction and "stripping"; centrifugation; vinyl chloride monomer reclaim; materials handling; PVC storage; and product bagging or bulk loading. In addition, there is a significant contribution from "fugitive" or "other" emissions. The pollutants are mostly hydrocarbon vapors and PVC fines. Relative to pollution significance, PVC projections to the year 1980 indicate a weighted SEI of about 4,840 units.

If PVC is considered for inclusion in the group of petrochemicals which may qualify for in-depth studies, a further factor should be considered. This factor has to do with the increasing prominence of the "bulk polymerization" process. The present report herewith does not reflect the possible influence of appreciable "bulk polymerization" capacity on the projected SEI. It may be determined that questionnaires should be issued to "bulk polymerization" PVC manufacturers if a decision is made to study PVC in-depth.

II. Process Description

This is a simplified description of four modern processes used to produce polyvinyl chloride. A simplified composite flow diagram is attached. Please see fold-out drawing No. R-225. A Net Material Balance is presented in Table I. Please see Table II relative to a gross heat balance.

1. Suspension Polymerization

About 78% of all PVC resins (both homopolymers and copolymers) produced in the United States in 1971 were produced by suspension polymerization. The polymerization is carried out in an aqueous system in which monomer droplets are maintained in suspension by means of a protective colloid in conjunction with brisk agitation. Typical protective colloids are polyvinyl alcohol, gelatin and substituted celluloses (e.g., carboxymethyl cellulose).

Generally, suspension polymerization is operated as a batch process employing glass-lined reactors (having a capacity of 2-6 thousand gallons in older plants and larger in newer plants). The reactor is first charged with deionized water, and then a protective colloid (0.05 to 2% of the weight of the monomer), a buffer (e.g., sodium acetate) and an initiator (e.g., lauryl peroxide, azobisisobutyronitrile, or isopropyl peroxydicarbonate) are added. The vinyl chloride and, in the case of copolymer production, the second monomer (e.g., vinyl acetate, propylene, or vinylidene chloride) are then intermittently introduced in controlled ratios. The mixture is then brought to the polymerization temperature (about 50° C) and, after variable induction periods depending on the initiator used, the polymerization starts. The heat of polymerization is removed from the system to maintain the desired reaction temperature. When lauryl peroxide is used as the initiator, the polymerization is substantially complete after a period of about 16 hours.

A dispersion of relatively large polymer particles in water is obtained by the suspension polymerization process. After unreacted monomer is driven out of the slurry and recovered, the slurry is centrifuged and the polymer is dried in a flash dryer, in which it is subjected to an air stream at about 80° C, complete drying usually required more than one passage. The dry polymer is screened, generally through a 40-mesh screen, and shipped in bulk or packed in multiwall paper bags.

2. Emulsion Polymerization

About 13% of the PVC resins produced in the United States in 1971 were produced by emulsion polymerization which is basically very similar to the suspension process except that relatively large amounts of emulsifying agents are used, usually in pairs where one agent is soluble in the monomer and the other in water. Such systems, combined with powerful agitation, very effectively prevent the coalescence of polymer particles and, as a result, resins of a very small particle size are obtained. The drying methods are also designed to maintain a small particle size; spray dryers are frequently used. Complete removal of emulsifiers is never achieved in resins produced by this process, so that articles of high clarity (as needed in packaging film) or of very low water absorption (as needed in wire insulation) cannot be produced from such resins. The generally higher price of emulsion-polymerized resins compared to that of suspension-polymerized resins is, nevertheless, accepted by users who need compounds in liquid form (fluid dispersions of PVC resins in plasticizers, called plastisols) for the manufacturing of end products. In the United States, all resins produced by emulsion polymerization are used for plastisols (and, to a minor extent, in latex form). In Europe, emulsion polymerization processes have been refined further than in the United States so that general purpose resins (useful for calendering and extrusion) are also produced there by variations of the emulsion process.

3. Bulk Polymerization

In this relatively new process, which was used to make 6% of the PVC resin produced in the United States in 1971, vinyl chloride is polymerized without the addition of other liquids. A two-stage version of the process is so attractive that it has been licensed all over the world (ECN, April 3, 1970, pa. 14).

In the two-stage bulk polymerization process, a suitably shaped reactor is provided for the initial liquid phase of the reaction, and a differently designed autoclave is then used to agitate the dry, powdery mass effectively until the conversion from monomer to polymer reaches a level of about 90%. Heat exchange is provided by the distillation of monomer and its recondensation within the reactor and external condensers. The rate of out-put of the two-stage bulk polymerization plants is said to be more than twice as high as that of a good suspension process plants of comparable size (i.e., with a comparable number and size of reactors). It is generally expected that two-stage bulk polymerization of vinyl chloride will be widely used world-wide in the next several years.

Bulk polymerized PVC resins resemble the suspension resins in appearance and are characterized by high particle uniformity and purity. This results in end products of unusually good optical clarity (important for packaging uses). Also, these resins have remarkably good heat stability and improved fusion properties, i.e., they can be processed with the ease of conventional vinyl chloride-vinyl acetate copolymers.

4. Solution Polymerization

Although solution polymerization is over 40 years old, only about 3% of the PVC resins produced in the United States in 1971 were produced by this method. In this process, the monomers are first dissolved in an organic solvent (such as n-butane or cyclohexane) in an autoclave. After the addition of a peroxide initiator and heating of the stirred solution to 40° C, polymerization begins and the polymer precipitates as the reaction proceeds.

Solution polymerization is used exclusively for the production of copolymers of vinyl chloride with vinyl acetate (usually those containing 10-25% acetate). These solution-polymerized copolymers are remarkably pure and uniform and their chief value lies in their unique solubility and film-forming characteristics. A greatly improved form of the original process is used for the production of these specialty coating resins.

5. Structure

In principle, addition of the vinyl chloride monomer units during polymerization can occur either in head-to-tail fashion, resulting in 1,3 positions for the chlorine atoms

$$-\!\!\left[\,CH_2CHClCH_2CHCl\,\right]\!\!-_n$$

or head-to-head, tail-to-tail, placing the chlorine atoms in 1,2 positions as follows:

$$-\!\!\left[\,CH_2CHClCHClCH_2\,\right]\!\!-_n$$

Three categories of end groups are possible in the polymer. Saturated groups are formed by chain transfer with monomer and polymer and by termination through disproportionation:

$$\sim\!\!\!\sim\!\!-CH_3;\quad \sim\!\!\!\sim\!\!-CH_2Cl;\quad \sim\!\!\!\sim\!\!-CHCl_2$$

Unsaturated chain ends are due to termination by disproportionation and to chain transfer to monomer:

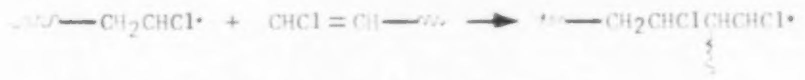
$$-CH_2CHClCH=CHCl;\quad -CCL=CH_2;\quad -CH_2CHClCH=CH_2$$

Initiator or solvent (chain-transfer agent) fragments, represented by R, can be incorporated in the terminal group:

$$-CH_2R;\quad -CHClR$$

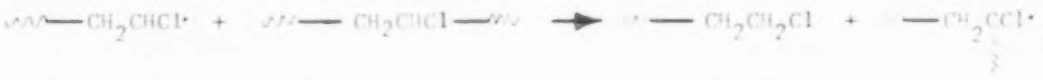
Due to the high transfer activity of the monomer, about 60% of the polymer molecules are estimated to have unsaturated end groups. For the same reason, the percentage of chain ends containing initiator fragments is low; the amount of solvent fragments depends upon its transfer activity.

Long-chain branching can be caused by the incorporation of the terminal double bond of a polymer molecule into a growing chain:



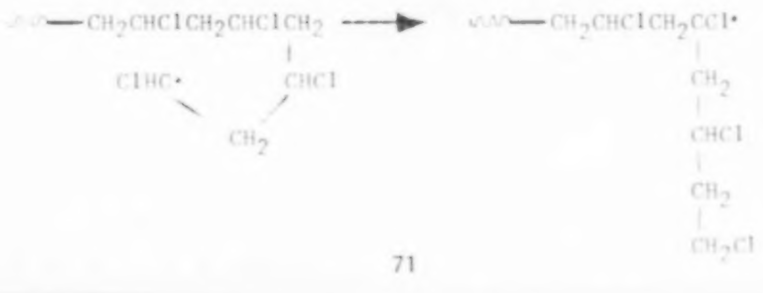
$$\sim\!\!\!\sim\!\!-CH_2CHCl\cdot + CHCl=CH\!-\!\!\sim\!\!\!\sim \longrightarrow \sim\!\!\!\sim\!\!-CH_2CHCl\underset{\wr}{C}HCHCl\cdot$$

or by intermolecular chain transfer to polymer:



$$\sim\!\!\!\sim\!\!-CH_2CHCl\cdot + \sim\!\!\!\sim\!\!-CH_2CHCl\!-\!\!\sim\!\!\!\sim \longrightarrow \sim\!\!\!\sim\!\!-CH_2CH_2Cl + \sim\!\!\!\sim\!\!-CH_2\underset{\wr}{C}Cl\cdot$$

Intramolecular chain transfer (back-biting) leads to the formation of short side chains:



6. PVC Product

Compounded PVC resins are converted to end products by several processes. Extrusion (employing mostly multiple-screw machines in Europe and mostly single-screw machines in the United States) is used to produce both rigid extrusions (e.g., pipe and conduit, siding and window sashes) and flexible extrusions (e.g., electrical wire insulation, garden hose, and packaging film). To feed a large extruder, preheated, mixed compound in chip form may be conveyed from storage or directly from a mixing extruder.

Extrusion lines are engineered for the types of products to be extruded, from electrical wire insulation to pipe of 18 inches diameter. The extruders are continuously fed with compound, which is either purchased or prepared in an on-site compounding plant. The approximate cost of a single extrusion line varies considerably depending on the size of the extruder, its type and the auxiliary equipment.

Rigid and flexible vinyl sheets are generally produced on four-roll calenders. The sheets may be combined with a fabric as it leaves the calender, or this may be done subsequently in a separate laminating step.

Todays calenders run widths usually to 72 inches and some as broad as 92 inches, and they produce film and sheet at rates averaging more than eight million pounds per year of compound (equivalent to 5.5-6 million pounds of resin), depending on thickness (e.g., 2.5 million pounds per year for light gauge rigid film, 4.5 million pounds per year for heavier flexible film and higher rates for flexible sheeting).

Dispersions or plastisols are used for fabric coating (either on knife machines, roller coaters, or casting machines), and in the production of a low-cost type of vinyl floor tile where plastisol is cast on a felt base. Plastisols are also used in rotational molding (e.g., for toys and traffic cones) and in the dipping and hot-spraying of tool handles and appliance parts.

The use of compression molding for PVC resins is restricted to the production of phonograph records. Injection molding of rigid PVC has been developed largely in the 1960s and is mostly employed in the production of pipe fittings, and to a much smaller extent in the production of parts for communications equipment, business machines and toys.

A complex and still emerging technology in the processing of compounded PVC resins is the blow-molding of containers.

III. Plant Emissions

A. Continuous Air Emissions

1. Reclaim Vents

All producers reclaim unreacted monomer. These operations can be one of the sources of air pollution in the production of PVC. The reported vent streams in this category, along with their pollution control devices, are summarized in Tables III and IV.

2. Drying and Materials Handling Losses

After the PVC solids are dried, they are most often transported in-plant via pneumatic conveying systems. The various atmospheric vents that are associated with these systems are a source of hydrocarbon and particulate emissions. With suitable retention means such as cyclones and bag filters, continuous particulate emissions are present, but relatively small in amount. Emission and control device data are summarized in Tables III and IV.

B. Intermittent Air Emissions

1. Routine In-Processing Venting

Some routine in-process venting is implicit where, for example, several batch-type reactors are operated in parallel. This venting has no significance relative to the SEI.

2. Start-Up and Emergency Vents

According to the questionnaire responses received, these vents go to atmosphere. The contribution to the SEI stemming from these sources is negligible.

C. Waste Water

Process waste water arises from sources such as centrifuging and VCM stripping. The used water is 1) given treatment in-house, or 2) is sent out for handling by others, off-site.

One respondent (27-4) reports the system in use as developed in cooperation with the U.S. EPA for demonstration of treatment methods for PVC waste waters. Reference - U. S. Government Printing Office, Project No. 12020 DJI.

D. Solid Wastes

1. Spent Catalysts

PVC catalysts do not pose a solid waste problem. Although the literature indicates numerous variations and nuances relative to PVC catalysts, the following explanation represents, in principle, the reason these catalysts pose no solid waste problem.

The ingredients for a batch are added to the reactor in controlled amounts and according to a programmed sequence. The catalyst or initiator present in the reagent mix has to decompose in order to start the polymerization reactions. There are no ensuing solid catalyst wastes from this procedure.

2. PVC Waste

PVC waste arises from such operations as centrifugation, vessel cleaning, screening and spillage. The material is disposed of via landfill or contract haulage.

E. Odors

No odors are indicated for normal on-stream conditions. One respondent indicates an in-plant odor in connection with polymerization operations when a venting need stems from an up-set condition. No off-plant odors are reported by any of the questionnaire respondents.

F. Fugitive Emissions

The respondents indicate fugitive emissions (= "other emissions") of significant proportions, as shown quantitatively in the tabular portions of this report. It is assumed for the purpose of this screening study that all PVC operations have significant fugitive emissions; for example, from agitator shaft seals; pump and compressor seals; valve stems, although some of these are small.

Liquid storage is 1) pressurized, or 2) low vapor pressure atmospheric tankage. The respondents are presumed to allot storage losses to "Other Emissions", Section VIII, of the questionnaires, which they, in general, have calculated from their overall material balance. The only itemized storage loss reported is ascribed to VAM (vinyl acetate monomer) storage, as indicated in the emissions listing tabulated in this report.

IV. Emission Control

The various emission control devices that have been reported as being employed by operators of polyvinyl chloride plants are summarized in the Catalog of Emission Control Devices, Table IV. A brief commentary on the devices currently employed is included below.

Cyclones

In polyvinyl chloride production, these devices are used to reduce the amount of PVC dust emitted from the pneumatic conveyor vent systems. The device efficiencies are characterized at 99.9+%, but the conclusion may be tentatively drawn that in the future some cyclone installations may be teamed up with or displaced by bag filters, based on the present predominence of bag filters for retention of air-born PVC fines.

Bag Filters

For retention of fines, bag filters appear to be the ultimate final-step device for the PVC plant of the future. A properly chosen device, according to published literature, will remove substantially all of any PVC particulate dust above approximately 50 microns particle size. The bag filters could be used alone, or as back-up for other devices such as cyclones, depending on the specific process requirements.

Flares and Incinerators

As reported elsewhere in this screening study, the net vents containing pollutants flow directly to the atmosphere, and PVC solids disposal avenues are via landfill or contract haulage. There are no flares or incinerators reported as dedicated entirely to PVC manufacturing facilities.

Compression and/or Cooling or Equivalent

Several respondents report as emission control devices systems based on compression and/or cooling via "vent condensers" to condense and retain components of process vents which would otherwise reach the atmosphere.

NOTE: A VCM distillation tower is shown by one respondent as an emission control device, but, although it is tabulated in Table IV for the sake of completeness, it is discounted here as a device "per se" for inclusion in future control schemes. The tower is required for the process economics, but the devices for emission control are ascribable categorically to the "vent condensers" following the towers main condenser.

V. Significance of Pollution

Based on the comments below, it is recommended that polyvinyl chloride be placed, at present, in a stand-by category relative to the petrochemicals which may qualify for in-depth study.

The methods outlined in Appendix IV of this report have been used to forecast the number of new polyvinyl chloride plants that will be built by 1980, and to estimate the total weighted annual emissions from these new plants. This work is summarized in Tables V, VI and VII.

The Table V forecast of new plants is based on the assumption that the PVC growth rate will project on average as an annual capacity increase of about 10 percent through 1980. A Significant Emission Index (SEI) of 4,840 has been calculated. See Table VII. Of this total, 4,240 units stem from hydrocarbon vapors. Total increased emissions (by 1980) of 63,000,000 lbs./year are envisioned, based on the Table VII figures of 53 MM lbs./year HC plus 10 MM lbs./year particulates.

If PVC qualifies later for an in-depth study, a further point appears to warrant consideration. The respondents "in tota" cover a wide spectrum with respect to assignment of emissions to 1) fugitive sources, and 2) all other sources. A significant portion of the reported emissions (to atmosphere) may be shown under "Fugitive" or "Other" labelling in one instance, whereas "Fugitive Emissions" may appear to account for only a small portion or "none" of the total in another instance. As a constituent of an in-depth study, it would seem that further definition and resolution of this picture is required.

Factors for consideration in nominating PVC for a future in-depth study involves the nature of the emitted particulates. The first of these is the fact that the material is inert. The second is the particle size distribution. One producer of PVC reports data indicating that the bulk of the particles in four separate samples of a suspension resin range between 100 and 250 microns, with only about 2 percent being smaller than 75 microns and 20 PPM (one sample only) being smaller than 15 microns. However, another producer, who admits he has no data, has estimated the drier dust to be "very fine - perhaps less than 20 microns".

VI. Polyvinyl Chloride Producers

The following tabulation of polyvinyl chloride producers indicates published production capacity.

Company	Location	Capacity - MM Lbs./Year
Air Products & Chemicals, Inc. (Plastics Division)	Calvert City, Ky.	120
	Pensacola, Florida	50
Allied Chemical Corp.	Painesville, Ohio	220
American Chemical Corp. (jointly owned by ARCO Chemical Company, division of Atlantic Richfield Co. and Stauffer Chemical Co.	Long Beach, Calif.	125
Borden Inc. Borden Chemical, division	Illiopolis, Ill.)	240
	Leominster, Mass.)	
Continental Oil Co. Conoco Plastics Div.	Aberdeen, Miss.	220
	Oklahoma City, Oka.	80
Diamond Shamrock Corp. Diamond Shamrock Chemical Co. subsidiary Plastics Division	Delaware City, Del.)	250
	Deer Park, Texas)	
Ethyl Corp. Industrial Chemicals Div.	Baton Rouge, La.	180
The Firestone Tire & Rubber Company Firestone Plastics Co. Division	Perryville, Maryland	130
	Pottstown Pa.	140
The General Tire & Rubber Company, Chemical/ Plastics Division	Ashtabula, Ohio	100
The B. F. Goodrich Co. B. F. Goodrich Chemical Company, Division	Long Beach, Calif.	125
	Henry, Illinois	125
	Louisville, Kentucky	275
	Avon Lake, Ohio	125
	Pedricktown, N. J.	130
The Goodyear Tire & Rubber Company Chemical Division	Plaquemine, La.	100
	Niagara Falls, N. Y.	100

Company	Location	Capacity - MM Lbs./Year
Great American Chemical Corp.	Fitchburg, Mass.	40
Keysor-Century Corp.	Saugus, Calif.	35
Monsanto Company Monsanto Polymers & Petrochemicals Co.	Springfield, Mass.	150
National Starch & Chemical Corp.	Meredosia, Ill.	10
Occidental Petroleum Corp. Hooker Chemical Corp., subsidiary Ruco Division	Burlington, N. J.	180
	Hicksville, N. Y.	10
Olin Corp. Thompson Plastics Co. Division	Assonet, Mass.	150
Pantasote Company	Passaic, N. J. Point Pleasant, W. Va.	120
Stauffer Chemical Co. Plastics Division	Delaware City, Del.	160
Tenneco Chemicals, Inc. (a major component of Tenneco Inc.) Tenneco Plastics Div.	Burlington, N. J.	165
	Flemington, N. J.	60
Union Carbide Corp. Chemicals & Plastics Div.	Texas City, Texas	200
	South Charleston, W. Va	120
Uniroyal, Inc. Uniroyal Chemical, Division	Painesville, Ohio	140
Total Capacity		4,375

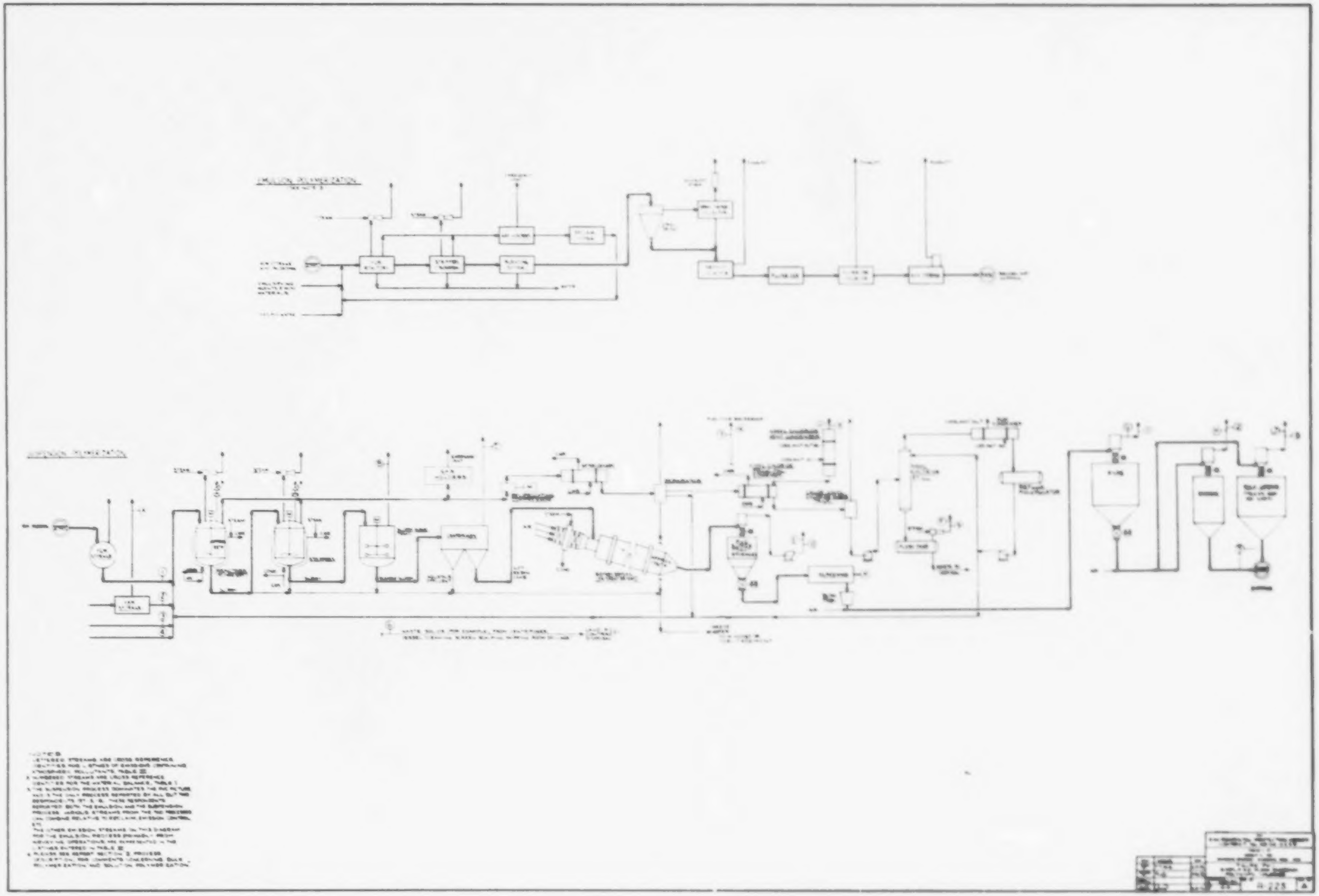

EMULSION POLYMERIZATION
SUSPENSION POLYMERIZATION

TABLE PV-I
COMPOSITE POLYVINYL CHLORIDE
NET MATERIAL BALANCE
(TONS/TON OF PVC CAPACITY)

INPUT	Stream No. on Simplified Flow Diagram	Polymer Ingredients	Other
Vinyl chloride monomer (VCM)	1	0.9700	
Vinyl acetate monomer (VAM)	2	0.0800	
Propylene	3	0.0038	
Initiators (catalysts)	4		0.0009
Suspending agents	4		0.0005
Surface active agents	4		0.0003
Plasticizers, where used	4	0.0001	
Total Input		1.0539	0.0017
OUTPUT			
PVC homopolymer and copolymer	5	1.0000	
Waste solids	6	0.0388	
Fugitive emissions	7	0.0020	
Monomer reclaim vent condenser	8	0.0010	
Residual VCM from vinyl Chloride still bottoms stream	9	0.0002	
Effluent from dryer collectors	10	0.0120	
Fines from silo collectors	11	0.0003	
Fines from baggers collectors	12	0.0001	
Fines from bulk loading collectors	13	0.0003	
Monomer storage		0.0009	
Total Output		1.0556	

TABLE PV-II
POLYVINYL CHLORIDE
GROSS HEAT BALANCE

The homopolymerization of vinyl chloride monomer occurs commercially according to four separate and distinct processes. There is one main reaction step in each of the four processes in which initiators (via free radical formation) induce the metamorphesis from monomer to polymer. Owing to the paucity of published information on the reaction thermal phenomena, however, there is no way to estimate suitably a gross heat balance from process information sources found in the public domain. However, the heat of polymerization is reported to be 650 BTU/lb.

TABLE PV-III
NATIONAL EMISSIONS INVENTORY
POLYVINYL CHLORIDE

Page 1 of 8

Company				
Location				
EPA Code No.	27-1	27-3		
Capacity - Tons of Polyvinyl Chloride/Yr.	37,500	50,000		
Average Production - Tons of PVC/Yr.	37,500	30,000		
Seasonal Range in Production - % of Max.	15	0		
Emissions to Atmosphere				
Stream - Letter on Flow Diagram	D	D	F	E
Description	Vinyl Chloride Vent Condenser	Vinyl Chloride Vent Condenser	Vinyl Chloride from Vinyl Chloride Still Bottoms	Dryer Collector Effluent
Flow - Lbs./Hr. of Pollutants	8	12	2	135
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow				
Composition - Ton/Ton of PVC				
Hydrocarbons	0.0008	0.0010	0.0002	0.0101**
Particulates				0.0016**
CO				
Sample Location	None	None	None	None
Date or Frequency of Sampling	Not Sampled	Not Sampled	Not Sampled	Not Sampled
Type of Analysis	None	None	None	None
Odor Present	No	No	No	No
Vent Stacks				
Flow - SCFM per stack	17.2	Not Indicated	Not Indicated	15,000
Number	1	1	1	3
Height - Feet	69	50	100	50
Diameter - Inches	3	1.5	1.5	24 x 24
Exit Gas Temperature - °F	65	30	290	130
Emission Control Device	None Indicated	Yes	Yes	Yes
Type - Flare				
Bag Filters				X
Cyclone				
Water Scrubber				
Other		Vent Condenser	Vinyl Chloride Still*	
Catalog I. D. Number		27-3.101	27-3.102*	27-3.103
Total Hydrocarbon Emissions - Ton/Ton PVC	0.0008	0.0010	0.0002	0.0101
Total Particulate - Ton/Ton PVC				0.0016
Total NO_x - Ton/Ton PVC				
Total SO_x - Ton/Ton PVC				
Total CO - Ton/Ton PVC				

*This entry is made in accordance with the respondent's labelling.

**From "Engineering Calculations and Plant Material Balance".

TABLE PV-III

NATIONAL EMISSIONS INVENTORY

POLYVINYL CHLORIDE

Page 2 of 8

Company					
Location					
EPA Code No.			27-3		
Capacity - Tons of Polyvinyl Chloride/Yr.			50,000		
Average Production - Tons of PVC/Yr.			50,000		
Seasonal Range in Production - % of Max.			0		
Emissions to Atmosphere					
Stream - Letter on Flow Diagram	C	H		J	K
Description	Silo Collector Fines	Bagger Collector Fines		Bulk Loading Collector Fines	Fugitive Emissions
Flow - Lbs./Hr. of Pollutants	4	1		3	
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous		Continuous	
if Intermittent - Hrs./Yr. Flow					
Composition - Ton/Ton of PVC					
Hydrocarbons					
Particulates	0.0003	0.0001		0.0003	0.0020
CO					
Sample Location	None	None		None	
Date or Frequency of Sampling	Not Sampled	Not Sampled		Not Sampled	
Type of Analysis	None	None		None	
Odor Present	No	No		No	
Vent Stacks					
Flow - SCFM per stack	***	500		1,500	
Number	***	3		2	
Height - Feet	75	30		30	
Diameter - Inches	8	8		8	
Exit Gas Temperature - °F	95	95		95	
Emission Control Device	Yes	Yes		Yes	
Type - Flare					
Bag Filters	X	X		X	
Cyclone					
Water Scrubber					
Other					
Catalog I. D. Number	27-3.104	27-3.105		27-3.106	
Total Hydrocarbon Emissions - Ton/Ton PVC					
Total Particulate - Ton/Ton PVC	0.0003	0.0001		0.0003	0.0020
Total NO_x - Ton/Ton PVC					
Total SO_x - Ton/Ton PVC					
Total CO - Ton/Ton PVC					

***4,500 SCFM total flow from 12 silos through 22 dust collectors

TABLE PV-III

NATIONAL EMISSIONS INVENTORY

POLYVINYL CHLORIDE

Page 3 of 8

Company					
Location					
EPA Code No.			27-4		
Capacity - Tons of Polyvinyl Chloride/Yr.			30,000		
Average Production - Tons of PVC/Yr.			30,000		
Seasonal Range in Production - % of Max.			0		
Emissions to Atmosphere					
Stream - Letter on Flow Diagram	D	E	None	G	H
Description	Vinyl Chloride Vent Condenser	Dryer Collector Effluent	"Day Storage" Collector Fines	Bulk Storage Collector Fines	Bagger Collector Fines
Flow - Lbs./Hr. of Pollutants	1	7	0.03	0.02	0.02
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow					
Composition - Ton/Ton of PVC					
Hydrocarbons	0.0002				
Particulates		0.0003	Negligible	Negligible	Negligible
CO					
Sample Location	None	None	None	None	None
Date or Frequency of Sampling	Not Sampled	Not Sampled	Not Sampled	Not Sampled	Not Sampled
Type of Analysis	None	None	None	None	None
Odor Present	No	No	No	No	No
Vent Stacks					
Flow - SCFM per stack	0.01	25,000	3,750	1,600	2,200
Number	1	1	1	1	1
Height - Feet	57	56	56	70	29
Diameter - Inches	1	26 x 46	13 x 14	9	10 x 10
Exit Gas Temperature - °F	45	150	100	100	85
Emission Control Device	None Indicated	Yes	Yes	Yes	Yes
Type - Flare					
Bag Filters			X	X	X
Cyclone					
Water Scrubber					
Other		U.O.P. Dust Collector			
Catalog I. D. Number		27-4 101	27-4 102	27-4 103	27-4 104
Total Hydrocarbon Emissions - Ton/Ton PVC	0.0002				
Total Particulate - Ton/Ton PVC		0.0003	Negligible	Negligible	Negligible
Total NO_x - Ton/Ton PVC					
Total SO_x - Ton/Ton PVC					
Total CO - Ton/Ton PVC					

TABLE PV-III
NATIONAL EMISSIONS INVENTORY
POLYVINYL CHLORIDE

Company						
Location						
EPA Code No.			27-5			
Capacity - Tons of Polyvinyl Chloride/Yr			47,500			
Average Production - Tons of PVC/Yr.			47,500			
Seasonal Range in Production - % of Max			0			
Emissions to Atmosphere						
Stream - Letter on Flow Diagram	B	C	E		D	F
Description	Slurry Tank Vent	Centrifuge Vent	Dryer Collector Effluent*****		Vinyl Chloride Vent Condenser	Fugitive Emissions
Flow - Lbs./Hr. of Pollutants	****	****	823		38	86.1
Flow Characteristic - Continuous or Intermittent	Intermittent	Intermittent	Continuous		Continuous	Continuous
If Intermittent - Hrs./Yr. Flow						
Composition - Ton/Ton of PVC						
Hydrocarbons			0.0599		0.0034	0.0075
Particulates			0.0022			
CO			0.0134			
Sample Location			None		None	
Date or Frequency of Sampling			Not Sampled		Not Sampled	
Type of Analysis			None		None	
Odor Present			No		No	
Vent Stacks			Rotary Kiln	Spray Dryer		
Flow - SCFM per stack	[illegible]	15	33,000	38,000		
Number	1	1	1	1		
Height - Feet	12	35	100	80		
Diameter - Inches	2	4	30 x 36	60		
Exit Gas Temperature - °F	160	150	180	140		
Emission Control Device	None	None	Yes	Yes	None	
Type - Flare						
Bag Filters						
Cyclone			E			
Water Scrubber						
Other				Dust Collector		
Catalog I. D. Number						
Total Hydrocarbon Emissions - Ton/Ton PVC	Negligible	Negligible	0.0599		0.0034	0.0075
Total Particulate - Ton/Ton PVC			0.0022			
Total NO_x - Ton/Ton PVC						
Total SO_x - Ton/Ton PVC						
Total CO - Ton/Ton PVC			0.0134			

****The combination of stream flow rate and vinyl chloride composition range (of 0.0 to 0.5 vol. %) indicated by the respondent give negligible emissions effects

*****Respondent 27-5 refers to "cyclones" on page 6 (a) and to "dust collector" on page 6 (f), but under "Section IV. Emission Control Device", he says "No emission control devices". If an in-depth study ensues relative to the 27-5 data, the definition of "emissions control device" should be reviewed with the respondent and the questionnaire data amended if necessary. Further, it should be noted that the "Dryer Collector Effluent" emission data are calculated (to the exclusion of sampling and test methods).

TABLE PV-III

NATIONAL EMISSIONS INVENTORY

POLYVINYL CHLORIDE

Page 5 of 8

Company								
Location								
EPA Code No.		27-6						
Capacity - Tons of Polyvinyl Chloride/Yr		45,000						
Average Production - Tons of PVC/Yr		45,000						
Seasonal Range in Production - % of Max		33.3						
Emissions to Atmosphere								
Stream - Letter on Flow Diagram	D	E,G,H,J						K
Description	Vinyl Chloride Vent Condenser	Collector Effluent Streams						Fugitive Emissions
Flow - Lbs./Hr. of Pollutants	9	******						10
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous						Continuous
if Intermittent - Hrs./Yr. Flow								
Composition - Ton/Ton of PVC								
Hydrocarbons	0.0009							0.0010
Particulates								
CO								
Sample Location	Sample Tape	None						
Date or Frequency of Sampling	As Needed	Not Sampled						
Type of Analysis	Orsat, Using Xylene	None						
Odor Present	No	None Indicated						
Vent Stacks		D	F	H	J	L	N	
Flow - SCFM per stack	3	27M	5M	1.4M	38.35M	5M	1.4M	
Number	1							
Height - Feet	70 above grade							
Diameter - Inches	2							
Exit Gas Temperature - °F	70 - 80	160	110	Ambient	160	110	Ambient	
Emission Control Device	Yes	Yes	Yes	Yes	Yes	Yes	Yes	
Type - Flare								
Bag Filters		X	X	X	X	X	X	
Cyclone								
Water Scrubber								
Other	Vent Condenser							
Catalog I. D. Number	27-6.101	27-6.102	27-6.103	27-6.104-110	27-6.111	27-6.112	27-6.113	
Total Hydrocarbon Emissions - Ton/Ton PVC	0.0009							0.0010
Total Particulate - Ton/Ton PVC								
Total NO_x - Ton/Ton PVC								
Total SO_x - Ton/Ton PVC								
Total CO - Ton/Ton PVC								

******Respondent 27-6 includes no stack information for these streams, and pollutant flows are indeterminate, since the compositions are based on PVC loadings and are not quantified.

TABLE PV-III
NATIONAL EMISSIONS INVENTORY
POLYVINYL CHLORIDE

Company			
Location			
EPA Code No.		27-7	
Capacity - Tons of Polyvinyl Chloride/Yr.		62,500	
Average Production - Tons of PVC/Yr.		61,700 (Estimated)	
Seasonal Range in Production - % of Max		7.7	
Emissions to Atmosphere			
Stream - Letter on Flow Diagram	E	G	F
Description	Dryer Collector Effluent	Silo Collector Effluent	"Stripping Vent"
Flow - Lbs./Hr. of Pollutants	9	0.3	10
Flow Characteristic - Continuous or Intermittent if Intermittent - Hrs./Yr. Flow	Continuous	Continuous	Continuous
Composition - Ton/Ton of PVC			
Hydrocarbons			0.0007
Particulates	0.0007	Negligible	
CO			
Sample Location	None	None	None
Date or Frequency of Sampling	Not Sampled	Not Sampled	Not Sampled
Type of Analysis	None	None	None
Odor Present	None Indicated	None Indicated	None Indicated
Vent Stacks			
Flow - SCFM per stack	54,000	1,500	"1,000 Lbs./Day (75% H_2O, balance VCM)"
Number	1	3 (guess)	1
Height - Feet	90	"65 - 82"	38
Diameter - Inches	32 x 42	"20 - 31"	3
Exit Gas Temperature - °F	130 - 150	"About Ambient"	212
Emission Control Device	Yes*******	Yes*******	
Type - Flare			
Bag Filters			
Cyclone			
Water Scrubber			
Other	"Dust Collector"	"Dust Collector"	
Catalog I. D. Number	*******	*******	
Total Hydrocarbon Emissions - Ton/Ton PVC			0.0007
Total Particulate - Ton/Ton PVC	0.0007		
Total NO_x - Ton/Ton PVC			
Total SO_x - Ton/Ton PVC			
Total CO - Ton/Ton PVC			

*******For in-depth study using 27-7 information, "Emission Control Device" definition would require clarification to the the respondent, since he reports for this category on the questionnaire: "Not Applicable".

TABLE PV-III
NATIONAL EMISSIONS INVENTORY
POLYVINYL CHLORIDE

Page 7 of 8

Company				
Location				
EPA Code No.			27-8	
Capacity - Tons of Polyvinyl Chloride/Yr.			70,000	
Average Production - Tons of PVC/Yr.			70,000 (Assumed)	
Seasonal Range in Production - % of Max.			0	
Emissions to Atmosphere				
Stream - Letter on Flow Diagram	A	B	E	E
Description	Vinyl Acetate Storage Vent	Reactor and Blend Tank Area Emissions	Dryer Collector Effluent	Dryer Collector Effluent
Flow - Lbs./Hr. of Pollutants	14 Ave.	281	8	10
Flow Characteristic - Continuous or Intermittent	Intermittent	Continuous********	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow	Not Indicated			
Composition - Ton/Ton of PVC				
Hydrocarbons	0.0009	0.0176		
Particulates			0.0005	0.0006
CO				
Sample Location	None	None	None	None
Date or Frequency of Sampling	Not Sampled	Not Sampled	Not Sampled	Not Sampled
Type of Analysis	None	None	None	None
Odor Present	Not Indicated	Not Indicated	Not Indicated	Not Indicated
Vent Stacks	None			
Flow - SCFM per stack		"1,681 Lbs./Hr."	"125,883 Lbs./Hr."	"132,010 Lbs./Hr."
Number		1	1	1
Height - Feet		60	20	20
Diameter - Inches		"0.6 Ft."	24	30
Exit Gas Temperature - °F		212	104	104
Emission Control Device	None	None	Yes	Yes
Type - Flare				
Bag Filters			X	
Cyclone				X
Water Scrubber				
Other				
Catalog I. D. Number			27-8.103	27-8.102
Total Hydrocarbon Emissions - Ton/Ton PVC	0.0009	0.0176		
Total Particulate - Ton/Ton PVC			0.0005	0.0006
Total NO_x - Ton/Ton PVC				
Total SO_x - Ton/Ton PVC				
Total CO - Ton/Ton PVC				

********If respondent 27-8 information becomes a contrubtion to in-depth study activities, this stream should be reviewed. The figures supplied in the questionnaire are determined by "engineering calculations and design flow sheet, plant material balances confirm".

TABLE PV-III

NATIONAL EMISSIONS INVENTORY

POLYVINYL CHLORIDE

Page 8 of 8

Company				
Location				
EPA Code No.	27-8			
Capacity - Tons of Polyvinyl Chloride/Yr.	70,000			
Average Production - Tons of PVC/Yr.	70,000 (Assumed)			
Seasonal Range in Production - % of Max.	0			
Emissions to Atmosphere				
Stream - Letter on Flow Diagram	B	D	D	E
Description	Reactor Area Emissions	Vinyl Chloride Vent Condenser	Vinyl Chloride Vent Condenser	Dryer Collector Effluent
Flow - Lbs./Hr. of Pollutants	41	Trace	Trace	9
Flow Characteristic - Continuous or Intermittent	Continuous*********	Continuous*********	Continuous	Continuous*********
if Intermittent - Hrs./Yr. Flow				
Composition - Ton/Ton of PVC				
Hydrocarbons	0.0026	Trace	Trace	0.0006
Particulates				
CO				
Sample Location	None	None	None	None
Date or Frequency of Sampling	Not Sampled	Not Sampled	Not Sampled	Not Sampled
Type of Analysis	None	None	None	None
Odor Present	Not Indicated	Not Indicated	Not Indicated	Not Indicated
Vent Stacks				
Flow - SCFM per stack	"4,671 Lbs /Hr."	"60 Lbs./Hr. Air"	"325 Lbs /Hr Air"	265,000 Lbs /Hr.
Number	1	1	1	1
Height - Feet	60	50	50	60
Diameter - Inches	4	1.5	1.5	48
Exit Gas Temperature - °F	212	78	78	104
Emission Control Device	None	Yes	Yes	Yes
Type - Flare				X
Bag Filters				
Cyclone				
Water Scrubber				
Other		Comp. & Cond.	Comp. & Cond.	
Catalog I. D. Number		28-8.104	28-8.101	28-8.105
Total Hydrocarbon Emissions - Ton/Ton PVC	0.0026			0.0006
Total Particulate - Ton/Ton PVC				
Total NO_x - Ton/Ton PVC				
Total SO_x - Ton/Ton PVC				
Total CO - Ton/Ton PVC				

*********Emulsion process emission.

TABLE PV-IV
CATALOG OF EMISSION CONTROL DEVICES
POLYVINYL CHLORIDE

Page 1 of 3

Device I. D. Number*	27-1 Respondent indicates for "Section IV, Emission Control Device": None	27-3.101	27-3.102	27-3.103
Purpose - Control Emission of		HC's	HC's	PVC Fines
Type		Vent Condenser	Distillation Tower	Bag Filter
Rate		12 lbs./hr.	4.5 GPM	45.000 SCFM
Installed Cost - Mat'l. & Labor - $	Elsewhere in the questionnaire information there are references to 1) vent condenser; 2) dust collectors.	5,000	75,000	94.500
Installed Cost - Mat'l. & Labor - ¢/lb. of PVC Production		0.005	0.075	0.0945
Operating Cost - Annual - $ (1972)		3,000	65,000 net credit	23.000
Operating Cost - ¢/lb. of PVC Production		0.003	0.065 net credit	0.023
Efficiency		83%	99.5%	99.8+% on particulate
Years Installed		1959	1959	59M 1959 35.5M 1965
Sources		Part of initial installation; manufacturer not indicated.	Shell by Wyatt; Trays by Koch	Mikro-Pulsaire (Pulverizing Machniery)

Device I. D. Number	27-3.104	27-3.105	27-3.106
Purpose - Control Emission of	PVC Fines	PVC Fines	PVC Fines
Type	Bag Filter	Bag Filter	Bag Filter
Rate	4,500 SCFM	1,500 SCFM	3.000 SCFM
Installed Cost - Mat'l. & Labor - $	49,000	23,500	10,000
Installed Cost - Mat'l. & Labor - ¢/lb. of PVC Production	0.049	0.0235	0.0100
Operating Cost - Annual - $ (1972)	7,000	12,000	2,600
Operating Cost - ¢/lb. of PVC Production	0.007	0.012	0.0026
Efficiency	99.9+%	99.9+%	99.9+%
Years Installed	35M 1959 14M 1965	15M 1959 8.5M 1965	1965
Sources	Flex-Kleen Corp.	Mikro-Pulsaire	Mikro-Pulsaire

*EPA code number for questionnaire respondent followed by emission control device number used by respondent.

TABLE PV-IV

CATALOG OF EMISSION CONTROL DEVICES

POLYVINYL CHLORIDE

Page 2 of 3

Device I. D. Number*	27-4.101	27-4.102	27-4.103	27-4.104	27-5 Respondent indicates for "Section IV Emission Control Device": No emission control devices He reports no cost figures relative to emission control device
Purpose - Control Emission of	PVC Fines	PVC Fines	PVC Fines	PVC Fines	
Type	Dust Collector	Bag Filter	Bag Filter	Bag Filter	
Rate	25,000 CFM	3,750 CFM	1,600 CFM	1,100 CFM	
Installed Cost - Mat'l. & Labor - $	48,568	7,663	4,892	4,237	
Installed Cost - Mat'l. & Labor - c/lb. of PVC Production	0.0809	0.0128	0.0082	0.0071	
Operating Cost - Annual - $ (1972)	400	1,150	1,000	850	
Operating Cost - c/lb. of PVC Production	0.0007	0.0019	0.0017	0.0014	
Efficiency	99+% over 44 microns	99.9+% over 44 microns	99.9+% over 44 microns	99.9+% over 44 microns	
Years Installed	1969	1969	1969	1969	
Sources	U.O.P. Dust Collector	Flex-Kleen Corp	Flex-Kleen Corp.	Flex-Kleen Corp.	

Device I. D. Number	27-6.101	27-6.102	27-6.103	27-6.104 through-110	27-6.111
Purpose - Control Emission of	HC's	PVC Fines	PVC Fines	PVC Fines	PVC Fines
Type	Vent Condenser	Bag Filter	Bag Filter	Bag Filter	Bag Filter
Rate	9 lbs./hr.	27,000 CFM design	5,000 CFM	1,400 CFM each of 7	38,350 CFM
Installed Cost - Mat'l. & Labor - $	3,500	57,500	12,000	3,500 each of 7	60,000
Installed Cost - Mat'l. & Labor - c/lb. of PVC Production	0.0039	0.0639	0.0133	0.0039	0.0667
Operating Cost - Annual - $ (1972)	20,500 credit	38,600 credit	43,400 credit	25,100 credit each of 7	37,500 credit
Operating Cost - c/lb. of PVC Production	0.0228 credit	0.0429 credit	0.0482 credit	0.0279 credit each of 7	0.0417 credit
Efficiency	96.3%	99.9% above 44 microns	99.9% above 44 microns	99.9% above 44 microns	99.9% above 44 microns
Years Installed	2.5M 1967 1.0M 1970	55.0M 1968 2.5M 1969	1968	17.5M 1968 7.0M 1970	1971
Sources	Process Engineering & Machine Co.	Flex-Kleen Corp.	Flex-Kleen Corp.	Fuller Co.	Pulverizing Machinery

*EPA code number for questionnaire respondent followed by emission control device number used by the respondent.

TABLE PV-IV

CATALOG OF EMISSION CONTROL DEVICES

POLYVINYL CHLORIDE

Page 3 of 3

Device I. D. Number*	27-6.112	27-6.113	27-7 Respondent	27-8.101	27-8.102
Purpose - Control Emission of	PVC Fines	PVC Fines	indicates for	HC's	PVC Fines
Type	Bag Filter	Bag Filter	"Section IV, Emission Control Device"	Condensation	Cyclones
Rate	5,000 CFM	1,400 CFM	Not Applicable	Trace	27,000 CFM
Installed Cost - Mat'l. & Labor - $	15,000	3,500		160,000	100,000
Installed Cost - Mat'l. & Labor - c/lb. of PVC Production	0.0167	0.0039	He reports no	0.1143	0.0714
Operating Cost - Annual - $ (1972)	42,800 credit	11,400 credit	cost figures	172,480	7,000
Operating Cost - c/lb. of PVC Production	0.0476 credit	0.0127 credit	relative to	0.1232	0.0050
Efficiency	99.9% above 44 microns	99.9% above 44 microns	emission control	Over 99%	"Measured 99.98%"
Years Installed	1971	1968	devices.	60M 1965 100M 1970	1970
Sources	Pulverizing Machinery	Fuller Co.		Not Indicated	Not Indicated

Device I. D. Number	27-8.103	27-8.104	27-8.105
Purpose - Control Emission of	PVC Fines	HC's	PVC Fines
Type	Bag Filter	Condensation System	Bag Filter
Rate	20,000 CFM	Trace	67,000 CFM
Installed Cost - Mat'l. & Labor - $	80,000	50,000	120,000
Installed Cost - Mat'l. & Labor - c/lb. of PVC Production	0.0571	0.0357	0.0857
Operating Cost - Annual - $ (1972)	20,000	38,000	22,000
Operating Cost - c/lb. of PVC Production	0.0143	0.0271	0.0157
Efficiency	99.9%	Over 99%	99.6%
Years Installed	1965	1967	1967
Sources	"Dustex"	Not Indicated	"Dustex"

*EPA code number for questionnaire respondent followed by emission control device number used by the respondent.

TABLE PV-V
NUMBER OF NEW POLYVINYL CHLORIDE PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added in 1980	Economic Plant Size	Number of New Units
4,375	95	4,280	7,100	8,000	3,720	150 Estimated	25

NOTE: All rates are in MM lbs./year.

TABLE PV-VI

EMISSION SOURCE SUMMARY

TON/TON POLYVINYL CHLORIDE

Emissions	Source: Monomer Storage Area	Reaction Stripping and "Slurry" or "Blend" Tank Areas	Centrifuge Area	Vinyl Chloride Vent Condenser	Dryer Collector Effluent ***	Vinyl Chloride from Vinyl Chloride Still Bottoms	Silo Collector Fines	Bagger Collector Fines	Bulk Loading Collector Fines	Fugitive Emissions	Total
Hydrocarbons	0.0009	*	**	0.0010	0.0100	0.0002				0.0020	0.0141
Particulates		*			0.0020		0.0003	0.0001	0.0003		0.0027
NO_x											0.00
SO_x											0.00
CO											

*These areas are not on report by five of the respondents. Of the remaining two respondents, one reports an intermittent vent which has negligible pollutant effect and the other's report indicates 0.0176 T hydrocarbons per 1.0 T polyvinyl chloride. For this survey report, it is considered that for a new, "clean", well-maintained installation the pollutant contribution for the areas indicated is negligible.

**One respondent (27-5) reports a finite flow which is so small that it is not significant until the fifth decimal place

***The (27-5) data are not applied here because the pollutant flows are from very small percent compositions applied to relatively large total flow rates. This includes, for example, 0.1 vol. % carbon monoxide in a total flow of 33,000 SCFM, giving an emission ratio of 0.0134 T CO/1.0 T polyvinyl chloride. It is presumed that future capacity will be installed with dryer systems which will not be found to exhibit any CO in the collector effluent stream

TABLE PV-VII
WEIGHTED EMISSION RATES

Chemical Polyvinyl Chloride

Process Polymerization (All Processes)

Increased Capacity by 1980 3,720 MM Lbs./Year

Pollutants	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions Units
Hydrocarbons	0.0141	53	80	4,240
Particulates	0.0027	10	60	600
NO_x	0.00	0	40	0
SO_x	0.00	0	20	0
CO	0.00	0	1	0

Significant Emissions Index = 4,840

Styrene

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Number of New Plants by 1980	Table ST-V
Emission Source Summary	Table ST-VI
Weighted Emission Rates	Table ST-VII

I. Introduction

Styrene is an important intermediate for the manufacture of polymeric materials. It is used extensively in the manufacture of plastics including polystyrene, rubber modified impact polystyrene, acrylonitrile-butadiene-styrene terpolymer, styrene-acrylonitrile copolymer and for the production of styrene-butadiene synthetic rubber.

Commercial production began on a small scale shortly before World War II. Today over five and one half billion pounds are produced a year. Styrene capacity is expected to grow to ten billion lbs./year by 1980.

The only commercial process to make styrene, which is in use today, is catalytic dehydrogenation of ethylbenzene. The styrene produced is of a high quality and can be polymerized into high grade polymer.

Emissions from styrene production are low in comparison with other processes surveyed. The emissions result from distillation column vents, fuel consumption, storage tank losses and miscellaneous leaks and spills.

II. Process Description

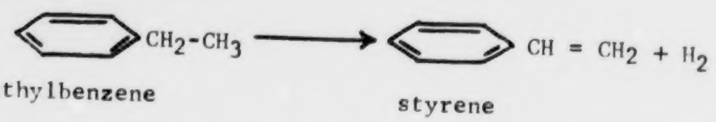
Direct dehydrogenation is the only commercial process currently employed for the manufacture of styrene. There are two major routes used to produce the monomer. The major one is the adiabatic process developed by Dow Chemical Company. Ethylbenzene is preheated with steam and by heat interchange to 520° C. Superheated steam, 710° C, and ethylbenzene vapors are fed into an adiabatic reactor at 650° C with a steam to ethylbenzene ratio of 2-3 to 1. Both ethylbenzene and styrene are subject to thermal decomposition at temperatures in excess of 610° C, but it is desirable to maintain temperatures approaching this figure to maximize conversion. The reactor contains a selective dehydrogenation catalyst such as zinc, chromium, iron or magnesium oxide. The catalyst operates continuously and has a long life (about one year). The steam serves the dual purpose of supplying heat to the reaction, which is endothermic by 540 - 570 BTU/lb. ethylbenzene converted and acting as a dilutant to bolster conversion, which would otherwise be low due to the volume change caused by the reaction. Conversion per pass is about 35 - 40% ethylbenzene reacted with yields of 90 - 92%. (See Figure ST-1)

The major difference between the isothermal reactor and the process described above lies in the means of supplying heat for the reaction. The isothermal process uses either heat exchange systems or flue gas to keep the reactants at a suitable temperature, about 585° C. It does have the advantages of lower steam consumption and less chance of thermal cracking. Conversions, yields and catalyst type are similar to the adiabatic process.

The reactor effluent is cooled first by incoming ethylbenzene and then by steam in heat exchangers. A condenser liquifies the steam, styrene, toluene, benzene and heavy products while the vent gases containing hydrogen, carbon dioxide and methane are sent to a recovery system. The non-condensables from this gas stream are used as fuel. The condensed material passes to a settling tank where the hydrocarbons are decanted and water is discharged to a disposal system.

The crude styrene is passed through a sulfur pot (sulfur acts as a polymerization inhibitor) and is then ready for vacuum distillation. Vacuum distillation is used to keep temperatures low and minimize polymerization of styrene. In most cases, the first distillation separates benzene, toluene and residual water as overhead product. The benzene and toluene are redistilled in a small column and stored. The ethylbenzene-styrene mixture from the first tower is then separated with ethylbenzene going overhead and recycled to the dehydrogenation step. The styrene bottoms containing about one percent ethylbenzene is ready for final finishing. This can be done either in batch stills or more often in a continuous distillation column. The overhead from this column is styrene and the bottoms tar, polymer and sulfur. Tert-butylcatechol is usually added to the styrene during final finishing and storage to retard polymerization.

The main reaction is:



but there is some "cracking" to benzene and toluene plus ethane, ethylene and methane.

Material and heat balances are given in Tables I and II, respectively.

III. Plant Emissions

A. Continuous Air Emissions

1. Distillation Vents

Non-condensibles and small amounts of condensible organic vapors are released from each of the three distillation columns employed in the process. Almost all respondents reported some kind of condensible vapor conservation system in use to recover valuable recycle materials and products. Since the type of system in use varies, the quantity of air emissions released would vary accordingly. More than half of the plants reported negligible pollutants from these vents.

Typically, light gases such as hydrogen, carbon dioxide and methane as well as small amounts of benzene, toluene and water are released from the benzene-toluene recovery column vent. Water and ethylbenzene are vented from the ethylbenzene recovery column vent. Small amounts of styrene and water were reported from the finishing column vent. A plant which listed no vapor recovery system had total hydrocarbon emissions of .00417 lbs./lb. styrene from the distillation section. The best operated recovery system reported zero emissions to the atmosphere from the columns.

2. Furnace Flue Gas

Fuel gas containing hydrogen, methane, CO_2 and organic vapors produced by the process is combined with natural gas and burned to provide the heat necessary to superheat the steam. Combustion is almost totally complete to CO_2 and H_2O. Only one plant reported any particulate products and the amount mentioned was small .00009 lbs./lb. styrene. NO_x formation is estimated to be 30 PPM, which is approximately .00002 lbs./lb. styrene. Low sulfur or zero sulfur natural gas is used in all cases.

3. Hydrogen Scrubber Vent

One plant 28-5 sells part of the hydrogen in the fuel gas as economics dictates. They employ a scrubber for this purpose. Only carbon dioxide and water are released from the scrubber vent.

4. Stripper Vent

Respondent 28-2 reports that a stripper is used before primary distillation, and emits .00096 lbs. of toluene/lb. of styrene, and .0032 lbs. of ethylbenzene/lb. of styrene, as well as water into the atmosphere through the stripper vent.

5. Storage Tank Vent

Losses due to storage vents are estimated to be 370,000 lbs./year by respondent 28-6. This amounts to .00067 lbs. of hydrocarbons/lb. styrene. Respondent 28-8 estimates his losses to be .00003 lbs. of hydrocarbons per lb. styrene. Obviously, the method of storage tank vapor conservation is the prime determining factor when studying tank losses.

B. Intermittent Air Emissions

1. Start-Up and Emergency Vents

During start-up or emergency conditions, gas from the reactor and/or the fuel gas stream are vented. These emergencies are reported to occur about two times a year for 2 - 36 hours. Emissions from the fuel gas emergency vent are reported on a yearly basis by respondent 28-9 to be .00003 lbs. of CO_2/lb. of styrene, negligible amounts of H_2 and methane and and .00051 lbs. of benzene, toluene and styrene/lb. of styrene. About half of the plants reported some kine of flare system to handle emergency emissions. In that case, carbon dioxide and water would be essentially the only emissions released under emergency conditions.

Reported air emissions and emission control data are summarized in Tables III and IV.

C. Waste Water

A large quantity of water is needed for process steam and for cooling purposes. In all cases the waste water is either treated on-site and reused or treated and discharged. Water requirements are summarized below.

EPA Code	Discharge Flow (GPM)	Treatment
28-2	No discharges	
28-3 (1)	0.5	Neutralization,filtration
	4.5	Untreated (cooling tower blowdown)
28-6 (1)	735	Treated and reused
28-7	350	Treated
28-8	65	Used in another process then treated.

(1) Combined waste water from benzene to ethylbenzene process and ethylbenzene to styrene process.

D. Solid Wastes

1. Spent Catalyst

About 500 lbs. of catalyst is disposed of for every million pounds of styrene capacity. The waste is usually sent to land fill.

2. Filter Aid

Respondent 28-5 reported disposal of 14,000 lbs./year of filter aid in sanitary land fill.

E. Odors

The production of styrene does not appear to present an odor problem. No respondent reported any odor complaints or serious odor problems.

F. Fugitive Emissions

Only respondent 28-3 provided any estimate of emissions due to pipe leaks and spills. The estimate provided is for a combined process making styrene directly from benzene. .00015 lbs. of hydrocarbons per lb. of styrene are emitted by the entire process.

G. Unreported Emissions

None of the respondents reported air emissions resulting from the disposal of the tarry residue from the styrene finishing column. It is believed that this stream contains most, if not all, of the sulfur added as a polymerization inhibitor, and that it might be incinerated. The emission of sulfur dioxide resulting from this operation has been estimated to be about 0.014 lbs./lb. of styrene which is equivalent to 140 million lbs. of sulfur dioxide per year by 1980. If this emission were to be considered in the calculation of a Significant Emission Index, it would increase the SEI by about 1200 units.

IV. Emissions Control

The emission control devices that have been reported as being employed by styrene producers are summarily described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calculate it have been made available. Three types of efficiencies have been calculated.

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutant in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{specific pollutants in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{(\text{pollutant} \times \text{weighting factor})\text{in} - (\text{pollutant} \times \text{weighting factor})\text{out}}{(\text{pollutant} \times \text{weighting factor}^{*})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor

Normally a combustion type device (i.e., incinerator, flare, etc) will be assigned both a "CCR" and a "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V.

Condensible Vapor Recovery

All respondents except for one report some vapor recovery system for organic vapors vented from the distillation columns. Their primary purpose is to recover valuable benzene, toluene and styrene but since these components would be vented to the atmosphere if not for the system, these devices are included in Table IV - Catalog of Emission Control Devices and described below.

Respondents 28-3, 28-7 and 28-8 use a combination condenser, steam ejector and hotwell system. Vapors vented from the overhead accumulator are condensed by heat exchange with cooling water. Most of the unrecovered vapors from the condenser are then recovered in the hotwell through steam ejection. Only small amounts of hydrocarbons vent from the hotwell. Efficiencies are high near 100% in most cases. Respondent 28-6 uses three condensers only. Although the details are not spelled out, no emissions are reported from the distillation area.

Flares

Flares are employed in a number of different areas in the various styrene plants reporting. Flares are used to burn gas vented from the reactor or fuel gas line in an emergency condition in plant 28-3, to burn irritating styrene vapors from the storage area in plant 28-5 and to burn unrecovered fuel gas in plant 28-6.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken. The reported emission data indicate that the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants.

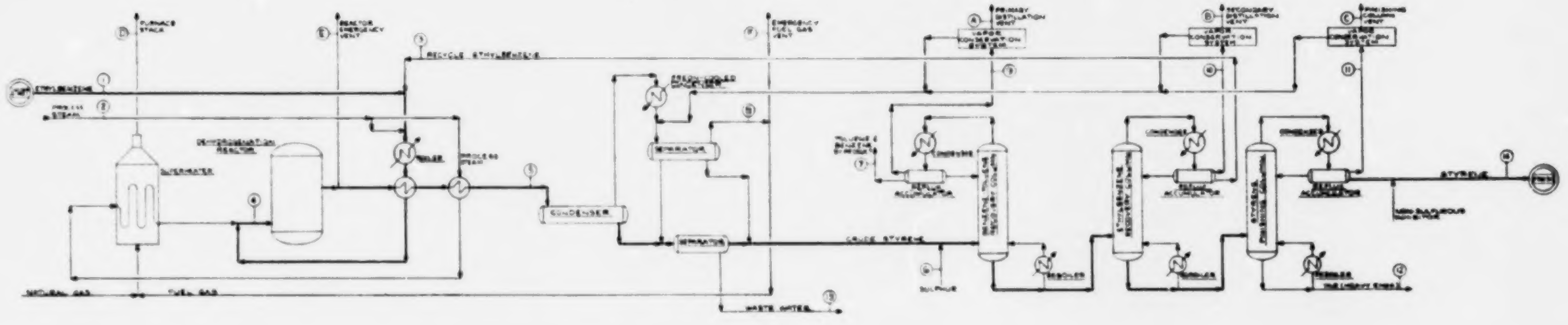
The Table V forecast of 1980 U. S. capacity is based upon information received from a Process Research Inc. report for the EPA. The expected growth rate for styrene is eight percent a year.

On a weighted emission basis a Significant Emission Index of 255 has been calculated in Table VII. This is substantially lower than the SEI's of other processes currently being surveyed. Hence, the recommendation to exclude an in-depth study of the subject process from the overall scope of work for this project.

VI. Styrene Producers

Producers (1)	Location	Capacity MM Lbs./Yr.
Amoco	Texas City, Texas	800
Cos-Mar	Carville, La.	530
Dow	Freeport, Texas	693.5
Dow	Midland, Michigan	350
El Paso	Odessa, Texas	120
Foster Grant	Baton Rouge, La.	720
Gulf	Donaldsville, La.	500
Monsanto	Texas City, Texas	1,300
Shell (2)	Torrance, Calif.	240
Sinclair-Koppers	Houston, Texas	110
Sinclair-Koppers	Kobuta, Pa.	200
Suntide	Corpus Christi, Texas	80
Union Carbide	Seadrift, Texas	310
Cosden (3)	Big Spring, Texas	(100)
		Total = 5,953.5

(1) Chem. Profiles, February 21, 1972
(2) Currently not operating
(3) Stand-by


FURNACE STACK
REACTOR EMERGENCY VENT
RECYCLE ETHYLBENZENE
ETHYLBENZENE
PROCESS STEAM
SUPERHEATER
DEHYDROGENATION REACTOR
BOILER
PROCESS STEAM
CONDENSER
NATURAL GAS
FUEL GAS
FREON-COOLED CONDENSER
SEPARATOR
SEPARATOR
EMERGENCY FUEL GAS VENT
WASTE WATER
CRUDE STYRENE
SULFUR
PRIMARY DISTILLATION VENT
VAPOR CONSERVATION SYSTEM
TOLUENE & BENZENE STORAGE
CONDENSER
REFLUX ACCUMULATOR
BENZENE TOLUENE RECOVERY COLUMN
REBOILER
ETHYLBENZENE RECOVERY COLUMN
CONDENSER
REFLUX ACCUMULATOR
REBOILER
SECONDARY DISTILLATION VENT
VAPOR CONSERVATION SYSTEM
STYRENE FINISHING COLUMN
CONDENSER
REFLUX ACCUMULATOR
REBOILER
TAR (HEAVY ENDS)
FINISHING COLUMN VENT
VAPOR CONSERVATION SYSTEM
STYRENE
NON SULFUROUS INHIBITOR
1
2
3
4
5
6
7
8
9
10
11
12
13
14
A
B
C
D
E
F

NOTES:
1. NUMBERED STREAMS ARE CROSS REFERENCE IDENTITIES FOR MATERIAL BALANCE AND CATALOG OF EMISSION CONTROL DEVICES TABLES I AND III
2. LETTERED STREAMS ARE CROSS REFERENCE IDENTITIES FOR NATIONAL EMISSIONS INVENTORY AND CATALOG OF EMISSION CONTROL DEVICES TABLES II AND IV.

ENVIRONMENTAL PROTECTION AGENCY
CONTRACT No. 68-02-0255

SIMPLIFIED FLOW DIAGRAM
STYRENE MONOMER PRODUCTION

NONE
R 231
A

TABLE ST-1
MATERIAL BALANCE
STYRENE PRODUCTION

Stream I. D. No.	1 & 2 Feed	3 Recycle Ethylbenzene	4 Total Feed	5 Reactor Effluent	6 Inhibitor	7 By-Product Toluene & Benzene	8 Fuel Gas	9, 10 & 11 Distillation Off-Gas (2)	12 Heavy Ends	13 Waste Water	14 Product
Ethylbenzene	1.1656	1.7484	2.9139	1.7487				.0003			
Methane				(.0042)			(.0042)				
Steam/Water (1)	8.0944	2.9140	8.0944	8.0944				.0029		8.0915	
Sulfur					.0070				.0070		
Styrene				1.0001				.0001			1.0000
Benzene				.0345		.0314		.0030		.0001	
Toluene				.0624 (.0002)		.0615	(.0002)	.0007		.0002	
Non-Aromatic				.0001				.0001			
Carbon Dioxide				.0297			.0294	.0003			
H_2				.0131			.0131				
Polymer				.0151					.0151		
Highboilers (Stilbene, etc.)				.0048					.0048		
Miscellaneous				.0011					.0011		
	9.2600	1.7484	11.0084	11.0084	.0070	.0929	.0469	.0074	.0280	8.0918	1.0000

(1) For adiabatic reactor.

(2) Organic vapors are usually condensed and returned to the system before this steam is released to the atmosphere.

TABLE ST-II
HEAT BALANCE (REACTOR SECTION) (1)
STYRENE PRODUCTION

Heat In

1) Enthalpy of ethylbenzene vapor (650° C) (2)	1,681
2) Enthalpy of steam (650° C)	13,452
Total =	15,133 BTU/Lb. of Ethylbenzene

Heat Out

1) Endothermic heat of reaction	570
2) Residual enthalpy of products (590° C) and steam	14,563
Total =	15,133 BTU/Lb. of Ethylbenzene

(1) For an adiabatic reactor.
(2) Base temperature - 25° C.

TABLE ST-III
NATIONAL EMISSIONS INVENTORY
STYRENE

Page 1 of 7

EPA Code No.			28-1			
Capacity - Tons of Styrene/Yr.			250,000			
Average Production - Tons of Styrene/Yr.			250,000			
Emissions to Atmosphere						
Stream I. D.	A	B	C		F_1 (1)	D
Stream	Primary Distillation Hotwell Vent	Secondary Distillation Hotwell Vent	Finishing Distillation Hotwell Vent	Hotwell Collection Vent	Emergency Flare Flue Gas	Furnace Flue Gas
Flow - Lbs./Hr.	82	6	5.5	>0	Confidential (2)	Confidential
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous		
if Intermittent - Hrs./Yr. of Flow						
Composition - Tons/Ton of Styrene						
Hydrogen	.00003					
Methane	.00005					
Ethylene						
Ethane						
Carbon Monoxide						
Carbon Dioxide	.00064					
Benzene	.00040			+		
Toluene	.00003			+		
Ethylbenzene		.00002		+		
Styrene			.00001	+		
Non Aromatics	00008					
Sulfur Dioxide						
Hydrogen Sulfide						
Nitrogen						
NO_x						
Water	.00008	00008	.00008	+		
Vent Stacks						
Number	1	1	1		1	1
Height - Ft.	16	16	16		275	175
Diameter - Inches	2	2	2		24	111.6
Exit Gas Temp. - F°	135	135	135		Unknown	480
SCFM/Stack	15.9	1.6	1.6			
Emission Control Devices						
Flare/Incinerator				No	Yes	
Refrigerator/Condenser	Yes	Yes	Yes			
Absorber/Scrubber						
Other						
Analysis	None	None	None	None		
Date or Frequency of Sampling						
Sample Tap Location						
Type of Analysis	Calc'd.	Calc'd.	Calc'd.	None		
Odor Problem	No	No	No	No		
Summary of Air Pollutants						
Hydrocarbons, Ton/Ton of Styrene			.00054			
Particulates, Ton/Ton of Styrene			0			
NO_x, Ton/Ton of Styrene			0			
SO_x, Ton/Ton of Styrene			0			
CO, Ton/Ton of Styrene			0			

(1) F_1 = flue gas from flare in stream F.
(2) Information about these streams was labeled confidential.

TABLE ST-III
NATIONAL EMISSIONS INVENTORY
SYTRENE

EPA Code No.	28-2
Capacity - Tons of Styrene/Yr.	650,000
Average Production - Tons of Styrene/Yr.	650,000

Emissions to Atmosphere				
Stream I. D.	A	B	(1)	D
Stream	Primary Distillation Vent	Secondary Distillation Vent	Stripper Vent	Furnace Flue Gas
Flow - Lbs./Hr.	950	100	400	472,000
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. of Flow				
Composition - Ton/Ton of Styrene				
Hydrogen				
Methane				
Ethylene				
Ethane				
Carbon Monoxide				
Carbon Dioxide	.00034			.19872
Benzene	.00189	.00010	.00096	
Toluene	.00042		.00032	
Ethylbenzene	.00037			
Styrene	.00012			
Non-Aromatics	.00009			
Sulfur Dioxide				
Hydrogen Sulfide	+			.00003
Nitrogen	.00131	.00049		2.2506
NO_x				.00035
Water	.00154	.00005	.00128	.46154
Oxygen	.00003			.11092
Vent Stacks	Not Specified	Not Specified	Not Specified	
Number				2
Height - Ft.				170
Diameter - Inches				120
Exit Gas Temp. - F°				540
SCFM/Stack				65,200
Emission Control Devices	No	No	No	No
Flare/Incinerator				
Refrigerator/Condenser				
Absorber/Scrubber				
Other				
Analysis		None	None	
Date or Frequency of Sampling	Once			6-9-72
Sample Tap Location	Not Specified			In Stream
Type of Analysis	Chromatograph	Calculated	Calculated	Unknown
Odor Problem	No	No	No	No

Summary of Air Pollutants	
Hydrocarbons - Ton/Ton of Styrene	.00427
Particulates - Ton/Ton of Styrene	0
NO_x - Ton/Ton of Styrene	.00035
SO_x - Ton/Ton of Styrene	.00003
CO - Ton/Ton of Styrene	0

(1) Stripper not shown in flow diagram, it preceeds primary distillation column

TABLE ST-III
NATIONAL EMISSIONS INVENTORY
STYRENE

Page 3 of 7

EPA Code No.	28-3							
Capacity - Tons of Styrene/Yr.	250,000							
Average Production - Tons of Styrene/Yr.	250,000							
Emissions to Atmosphere								
Stream I. D.	A	B	C		E	F1	D	
Stream	Primary Distillation Hotwell Vent	Secondary Distillation Hotwell Vent	Finishing Column Hotwell Vent		Reactor Emergency Vent	Emergency Fuel Gas Flare	Furnace Flue Gas	Fugitive Emissions
Flow - Lbs./Hr.	>0	.0017	.0029		Unknown	Not Specified	24,025	9.6 (3)
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous		Intermittent	Intermittent	Continuous	Intermittent
If Intermittent - Hrs./Yr. Flow					.02	Not Specified		8700
Composition - Tons/Ton of Styrene								
Hydrogen							( )	
Methane							(.00011)	
Ethylene							( )	
Ethane								
Carbon Monoxide								
Carbon Dioxide						+	.14416	
Benzene	+	+	+		+			( )
Toluene	+	+	+		+			( )
Ethylenebenzene	+	+			+			(.00008)
Styrene	+	+	+		+			( )
Non-Aromatics								( )
Sulfur Dioxide							+	
Hydrogen Sulfide								
Nitrogen								
NO_x							.00098	
Water					+	+	.23904	
Particulate							.00009	
Formaldehyde							.00001	
Vent Stacks					No	Not Specified		No
Number	1	1	1				1	
Height - Ft.	30	30	30				125	
Diameter - Inches	2	2	2				111.6	
Exit Gas Temp. - F°	120	114	114				500	
SCFM/Stack	>0	>0	>0				23,200	
Emission Control Devices					No		No	No
Flare/Incinerator						Yes		
Refrigerator/Condenser	Yes	Yes	Yes					
Absorber/Scrubber								
Other								
Analysis	None	None	None		Yes	None	None	None
Date or Frequency of Sampling					Daily (2)			
Sample Tap Location					In Stream			
Type of Analysis	Calculated	Liquid Sampling	Calculated		Liq.-Gas Chroms.		Calc'd. (1)	Calculated
Odor Problem	No	No	No		No	No	No	No
Summary of Air Pollutants								
Hydrocarbons - Ton/Ton of Styrene				.00020				
Particulates - Ton/Ton of Styrene				.00009				
NO_x - Ton/Ton of Styrene				.00098				
SO_x - Ton/Ton of Styrene				0				
CO - Ton/Ton of Styrene				0				

(1) Respondent used public health service publication No. 999-AP-42.

(2) Sampled under non-emergency conditions only.

(3) Estimated by Houdry based on respondents information.

TABLE ST-III
NATIONAL EMISSIONS INVENTORY
STYRENE

Page 4 of 7

EPA Code No.	28-5				
Capacity - Tons of Styrene/Yr.	346,750				
Average Production - Tons of Styrene/Yr.	346,750				
Emissions to Atmosphere					
Stream I. D.		F		D	
Stream		Reactor Emergency Vent	H_2 Scrubber Vent (3)	Furnace Flue Gas (5)	Storage Losses to Flare - Products
Flow - Lbs./Hr.		(1)	1,399	(6)	(8)
Flow Characteristic - Continuous or Intermittent		Intermittent	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow		Not Specified			
Composition - Ton/Ton Styrene					
Hydrogen		.000004			
Methane		+			
Ethylene					
Ethane		+			
Carbon Monoxide		.			
Carbon Dioxide		.000009	.00378	(7)	(9)
Benzene		.000002			
Toluene					
Ethyl Benzene		.000007			
Styrene		.000004			
Non-Aromatics					
Sulfur Dioxide					
Hydrogen Sulfide					
Nitrogen				+	
NO_x				+	
Water		.0000074	.01390	(7)	(9)
Particulate					
Vent Stacks					None
Number		4	1	27	
Height - Ft.		75	30	67	
Diameter - Inches		20	3	36	
Exit Gas Temp - F°		50	100	500	
SCFM/Stack		380	429	1350	
Emission Control Devices		No		No	
Flare/Incinerator					Yes
Refrigerator/Condenser					
Absorber/Scrubber			Yes		
Other					
Analysis		Yes (2)	None	None	Yes
Date or Frequency of Sampling		Infrequently			Continuous
Sample Tap Location		Compressor Line			
Type of Analysis		Chromatograph			Chromatograph
Odor Problem		No	No	No	No (11)
Summary of Air Pollutants					
Hydrocarbons - Ton/Ton of Styrene	.00002				
Particulates - Ton/Ton of Styrene	0				
NO_x - Ton/Ton of Styrene	Negligible				
SO_x - Ton/Ton of Styrene	0				
C - Ton/Ton of Styrene	0				

(1) 23,362 lbs./yr.
(2) Sampled under normal operating conditions.
(3) From H_2 scrubber which is before distillation system (not shown on flow diagram).
(4) Flow is variable depending on H_2 customer needs (average flow rate given).
(5) Furnaces burn both fuel gas and liquid wastes.
(6) Fuel consumption is confidential not enough information given to calculate quantity of combustion products, 0% sulfur fuel used, therefore, complete combustion to CO_2 and H_2O assumed.
(7) Relative amounts of CO_2 and H_2O depends on fuel requirements.
(8) Variable depending on rate of tank filling.
(9) Complete combustion to H_2O and CO_2 assumed.
(10) Continuous sampling for styrene vapors.
(11) Could present eye irritation problem if styrene is not monitered carefully.

TABLE ST-III
NATIONAL EMISSION INVENTORY
STYRENE

Page 5 of 7

EPA Code No.	28-6		
Capacity - Tons of Styrene/Yr.	265,000		
Average Production - Tons of Styrene/Yr.	265,000		
Emissions to Atmosphere			
Stream I. D.		D	
Stream	Incineration Products, Unrecovered Fuel Gas Flare	Furnace Flue Gas	Tank Losses
Flow - Lbs./Hr.	855 (1)	19,779	44.6
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous
If Intermittent - Hrs./Yr. Flow			
Composition - Tons/Ton of Styrene			
Hydrogen			
Methane			
Ethylene			
Ethane			
Carbon Monoxide	.00943		
Carbon Dioxide		.13510	
Benzene			( )
Toluene			( )
Ethyl Benzene			(00067)
Styrene			( )
Non-Aromatics			( )
Sulfur Dioxide			
Hydrogen Sulfide			
Nitrogen			
NO_x		.00002	
Water	.00339	.16150	
Vent Stacks	(2)	Not Specified	None
Number	1		
Height - Ft	175		
Diameter - Inches	16		
Exit Gas Temp. - F°	Unknown		
SCFM/Stack	636 (3)		
Emission Control Devices		No	
Flare/Incinerator	Yes		
Refrigerator/Condenser	Yes		
Absorber/Scrubber			
Other			
Analysis	None	None	None
Date or Frequency of Sampling			
Sample Tap Location			
Type of Analysis	Calculated		Estimate
Odor Problem	None	None	None
Summary of Air Pollutants			
Hydrocarbons - Ton/Ton of Styrene		.00067	
Particulates - Ton/Ton of Styrene		0	
NO_x - Ton/Ton of Styrene		.00002	
SO_x - Ton/Ton of Styrene		0	
CO - Ton/Ton of Styrene		0	

(1) Based on total conversion of unrecovered fuel gas to CO_2 and H_2O.
(2) Flare is used for incineration of vapors from other processes also.
(3) Total from all processes.
(4) Complete combustion to CO_2 and H_2O. NO_x concentration is approximately 30 PPM.

TABLE ST-III
NATIONAL EMISSIONS INVENTORY
STYRENE

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EPA Code No.	28-7			
Capacity - Tons of Styrene/Yr.	100,000			
Average Production - Tons of Styrene/Yr.	100,000			
Emissions to Atmosphere				
Stream I. D.	A			D
Stream	Distillation Hotwell Vent	Atmospheric Distillation Breather Vents	Fugitive Emissions; A.P.I Sump Section	Furnace Flue Gas
Flow - Lbs./Hr.	>0	>0	.5	10,656
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
If Intermittent - Hrs./Yr. Flow				
Composition - Ton/Ton of Styrene				
Hydrogen				
Methane				
Ethylene				
Ethane				
Carbon Monoxide				
Carbon Dioxide				.18924
Benzene	+	+	( )	
Toluene	+	+	( )	
Ethyl Benzene	+	+	(.00002)	
Styrene	+		( )	
Non-Aromatics				
Sulfur Dioxide				
Hydrogen Sulfide				
Nitrogen				
NO_x				.00002
Water				.23700
Vent Stacks				
Number	1	2	No	Not Specified
Height - Ft.	30	40, 60		
Diameter - Inches	6	3, 2		
Exit Gas Temp. - F°	100	100, 100		
SCFM/Stack				
Emission Control Devices		No	No	No
Flare/Incinerator				
Refrigerator/Condenser	Yes			
Absorber/Scrubber				
Other				
Analysis	None	None	None	None
Date or Frequency of Sampling				
Sample Tap Location				
Type of Analysis				
Odor Problem	No	No	NO	NO
Summary of Air Pollutants				
Hydrocarbons - Ton/Ton of Styrene		.00002		
Particulates - Ton/Ton of Styrene		.00002		
NO_x - Ton/Ton of Styrene		0		
SO_x - Ton/Ton of Styrene		0		
CO - Ton/Ton of Styrene		0		

TABLE ST-III
NATIONAL EMISSIONS INVENTORY
STYRENE

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EPA Code No.		28-8			
Capacity - Tons of Styrene/Yr.		155,000			
Average Production - Tons of Styrene/Yr.		155,000			
Emissions to Atmosphere					
Stream I. D.	A, B & C	E		D	
Stream	Distillation Vacuum Jet Exhaust	Emergency Fuel Gas Vent		Furnace Flue Gas	Storage Losses
Flow - Lbs./Hr.	3000	6,800		11.555 (1)	1,330
Flow Characteristic - Continuous or Intermittent	Continuous	Intermittent		Continuous	Continuous
if Intermittent - Hrs./Yr. Flow		25			
Composition - Tons/Ton of Styrene					
Hydrogen		+			
Methane		+			
Ethylene					(.00094)
Ethane					
Carbon Monoxide					
Carbon Dioxide				.10644	
Benzene	+	.00002			
Toluene		.00030			
Ethylbenzene	+	.00004			
Styrene	+	.00013			
Non-Aromatics	+	.00004			00003
Sulfur Dioxide					
Hydrogen Sulfide					
Nitrogen					
NO_x				.00002	
Water	.08013			.20211	
Vent Stacks		Not Specified			No
Number	1			1	
Height - Ft.	137.6			96.5	
Diameter - Inches	96			48	
Exit Gas Temp. - F°	690			835	
SCFM/Stack	60,000			30,000	
Emission Control Devices		No			
Flare/Incinerator					
Refrigerator/Condenser	Yes				
Absorber/Scrubber					
Other					
Analysis					
Date or Frequency of Sampling	None	Approximately 2 times/year		None	None
Sample Tap Location		Not Specified			
Type of Analysis		Chromatograph & Mass Spectrometer			
Odor Problem		Yes			
Summary of Air Pollutants					
Hydrocarbons - Ton/Ton of Styrene			.00054		
Particulates - Ton/Ton of Styrene			0		
NO_x - Ton/Ton of Styrene			.00002		
SO_x - Ton/Ton of Styrene			0		
CO - Ton/Ton of Styrene			0		

TABLE ST-IV
CATALOG OF EMISSION CONTROL DEVICES
STYRENE PRODUCTION

Page 1 of 2

VAPOR CONSERVATION DEVICES					
EPA Code No. for plant using	28-1	28-3	28-3	28-3	28-5
Flow Diagram - Stream I. D.	9,10 & 11	9	10	11	9,10 & 11
Device I. D. No.	VC-I	VC-II A	VC-II B	VC-II C	VC-III
Control Emission of	Organic Vapors	Organic Vapors	Organic Vapors	Organic Vapors	Organic Vapors
Units in System	Not Specified				Confidential
Compressor	↓				↓
Condenser	↓	Yes	Yes	Yes	↓
Number	↓	1	3	3	↓
Cooling Liquid	↓	Water	Water	Water	↓
Coolant Flow Rate	↓	Not Specified	Not Specified	Not Specified	↓
Temp. to Condenser - F°	↓	142	136	115	↓
Temp. out of Condenser - F°	↓	Not Specified	Not Specified	Not Specified	↓
K. O. Drum	↓				↓
Steam Ejector	↓	Yes	Yes	Yes	↓
Stages	↓	1	1	1	↓
Hotwell	↓	Yes	Yes	Yes	↓
Liquid Recovered - GPM	↓	Not Specified	Not Specified	Not Specified	↓
Non-Condensibles - SCFM	↓	.70	.0001	.0004	↓
Installed Cost - Mat'l. & Labor - $	↓	17,380	14,600	19,200	↓
Installed Cost based on - "year" - dollars	↓	1970	1970	1970	↓
Installed Cost - ¢/lb. of Styrene	↓	.0035	.0029	.0038	↓
Operating Cost - Annual - $ - (1972)	↓	Not Specified	Not Specified	Not Specified	↓
Value of Recovered Products - $/Yr.	↓	↓	↓	↓	↓
Net Operating Cost - Annual - $	↓	↓	↓	↓	↓
Net Operating Cost - ¢/lb. of Styrene	↓	↓	↓	↓	↓
Efficiency - % - SE		Near 100%	Near 100%	Near 100%	100%
Efficiency - % - SERR		Near 100%	Near 100%	Near 100%	100%

INCINERATION DEVICES				
EPA Code No. for plant using	28-1	28-3	28-5	28-5
Flow Diagram (Fig. I) Stream I. D.	11	F	Pad Gas Incinerator	Marine Storage Incinerator
Device I. D. No.	FL-I	FL-II	FL-III	FL-IV
Type of Compound Incinerated	Organic Vapors (2)	Fuel Gas Vent (Emergency Conditions)		
Type of Device - Flare	+	+	+	
Incinerator				
Other				
Material Incinerated - SCFM (lb./hr.)		Intermittent	≥ 0	≥ 0
Auxilliary Fuel Req'd. (excl. pilot)	Confidential (3)	No	No	No
Type	↓			
Rate - BTU/hr.	↓			
Device or Stack Height - Ft.	↓	150	Not Specified	Not Specified
Installed Cost Mat'l. & Labor - $	↓	(4)	Confidential	Confidential
Installed Cost based on - "year" - dollars	↓	↓	↓	↓
Installed Cost - ¢/lb. of Styrene	↓	↓	↓	↓
Operating Cost - Annual - $ - (1972)	↓	↓	↓	↓
Operating Cost - ¢/lb. of Styrene	↓	↓	↓	↓
Efficiency - % - CCR		100%	100%	100%
Efficiency - % - SERR		100%	100%	100%

(1) Benzene, toluene, ethylbenzene, styrene
(2) Mostly styrene
(3) Information about this device is confidential
(4) Flare is used primarily for other processes. It is impossible to calculate percentage cost attributable to styrene production.

TABLE ST-IV
CATALOG OF EMISSION CONTROL DEVICES
STYRENE PRODUCTION

Page 2 of 2

VAPOR CONSERVATION DEVICES					
EPA Code No. for plant using	28-6	28-6	28-7	28-8	28-8
Flow Diagram - Stream I. D.	9,10 & 11	Condensible Recovery from Stream 8 (3)	9,10 & 11	9,10 & 11	Condensible Recovery from Stream 8 (3)
Device I. D. No.	VC-IV	VC-V	VC-VI	VC-VII	VC-VIII
Control Emission of	Organic Vapors (1)	Organic Vapors	Organic Vapors	Organic Vapors	Organic Vapors
Units in System					
Compressor		Yes			Yes
Condenser	Yes	Yes	Yes	Yes	Yes
Number	3	2	3	4	2
Cooling Liquid	Water	Water	Water	Brine	Water-Brine
Coolant Flow Rate - GPM	140 (Total)	534 (Total)	Not Specified	642 (Total)	280 water - 548 brine
Temp. to Condenser - F°	350	100		140	120
Temp. out of Condensor - F°					
K. O. Drum		Yes			
Steam Ejector			Yes	Yes	
Number			3	3	
Steam Rate					
Hotwell			Yes	Yes	
Liquid Recovered - GPM	4	Not Specified	Not Specified	16	8
Non-Condensibles - SCFM	13 SCFM	450 SCFM	↓	13 SCFM	
Installed Cost - Mat'l. & Labor - $	8,000	375,000		59.900	161,573
Installed Cost based on - "year" - dollars	1968	1968		1964	1964
Installed Cost - ¢/lb. of Styrene	.0015	.071		.019	.052
Operating Cost - Annual - $ - (1972)	1160	182,250		4,000	11,377
Value of Recovered Product - $/Yr.	44,700	2,424,000		1,600,000	470,000
Net Operating Cost - Annual - $	(43,540)	(2,241,700)		(1,596,000)	(458,623)
Net Operating Cost - ¢/lb. of Styrene	(.0082)	(.42)		(.51)	(.15)
Efficiency - % - SE	100%	95%	—	Near 100%	97.6%
Efficiency - % - SERR	100%	95%	—	Near 100%	97.6%

INCINERATION DEVICES	
EPA Code No. for plant using	28-6
Flow Diagram (Fig. 1) Stream I. D. No.	Not on Flow Diagram
Device I. D. No.	FL-V
Type of Compound Incinerated	Unrecovered Fuel Gas
Type of Device - Flare	Yes
Incinerator	
Other	
Materials Incinerated SCFM (lb./hr.)	450 SCFM
Auxiliary Fuel Req'd. (excl. pilot)	No
Type	
Rate - BTU/hr.	
Device or Stack Height - ft.	175
Installed Cost Mat'l. & Labor - $	(4)
Installed Cost - based on "year" - dollars	↓
Installed Cost - ¢/lb. of Styrene	
Operating Cost - Annual - $ (1972)	
Operating Cost - ¢/lb. of Styrene	
Efficiency - % - CCR	—
Efficiency - % - SERR	—

---

(1) Benzene, toluene, ethylbenzene and styrene.
(2) According to information received
(3) Respondent claims this as an emission control device, actually he is just recovering valuable condensibles from a stream that would be combusted anyway.
(4) Flare also used for other processes, no breakdown given.

TABLE ST-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
5,953.5	240	5,713.5	10,000	10,000	4,286.5	500	8 - 9

Styrene-Butadiene Rubber

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I. Introduction

Rubber is one of the most important basic raw materials of industry. Prior to World War II nearly all the rubber used in the U. S. came from the great rubber tree planations of the Far East, located mainly in British Malaya and the Dutch East Indies. With the advent of WW II these sources of natural rubber became unavailable and the U. S. Government inaugurated a Government Synthetic Rubber Program, which quickly established a vast industry for the manufacture of synthetic rubber from styrene and butadiene (SBR). The plants, which were built under the auspices of this program, have constituted the backbone of the rubber industry to this day. (A list of the original plants and related pertinent data is presented in Table II of this report.)

The old government rubber plant technology was based on emulsion polymerization, and that is still the dominant method of producing SBR. Other methods (and other rubbers) are assuming ever greater importance, but they have not yet surpassed that method upon which the industry was founded.

There are five main sources of air pollution associated with the subject process. They are:

(1) Butadiene absorber vent gases.

(2) Dryer exhaust gases.

(3) Carbon black emissions from masterbatching operations.

(4) Talc from rubber bale dusting (during final packaging operations).

(5) Fugitive emissions.

Additionally, fairly large quantities of waste water are produced. However, in general, the process may be characterized as a low (air) polluter. This is due in part to the very low growth rate of the industry.

Today's estimated U.S. SBR production capacity is 4.5×10^9 lbs./yr. 1980 capacity is predicted to be 5.2×10^9 lbs./yr.

II. Process Description

Although most of the SBR made today is still produced in the rubber plants built in the 1940's, the production methods have undergrone almost continual evolution. The 'original' process involved batch polymerization at 122° F. Most of the SBR made today is 'cold rubber'...polymerized at 41° F, with the polymerization being carried out continuously. Modern oil and carbon black masterbatching techniques provide synthetic rubbers that are, in most respects, significantly better than natural rubber. The following process description may be more easily followed by referring to the flow diagram presented in Figure I:

Fresh styrene is stored in 30,000 gallon horizontal steel tanks, or in larger (and more modern) floating roof tanks of up to 650,000 gallons capacity. Butadiene may be stored in tanks or spheres of from 30,000 to 600,000 gallon capacity, although many plants receive butadiene by pipeline and have no storage facilities for it. Fresh styrene is mixed with recycle styrene, cooled and pumped into the bottom of the first of a series of stirred polymerization reactors. Fresh butadiene is mixed with recycle butadiene, sometimes caustic washed (to remove polymerization inhibitors from the fresh butadiene), chilled and pumped to the bottom of the first polymerization reactor. Additionally, soap, water and various modifying and activating agents are also pumped into the first reactor simultaneously with the addition of styrene and butadiene. The flow rates of all components must be carefully regulated to assure that the proper proportioning of 'recipe' components is achieved. (See Table I for typical recipes.) All components are added continuously.

Most plants still use modified versions of the original 3,750 gallon glass-lined batch reactors. The reactors are now connected in series with the inlets in the bottom and the outlets at the top. Agitation is provided by suspended, three bladed impellors. Heat removal and temperature control (at 41° F) is accomplished thru refrigerated jacketing. Following the battery of agitated reactors is a 'displacement reactor' section, which is essentially a long, large diameter pipe, possibly 18" x 300' long, usually subdivided into a series of shorter sections. Polymerization is halted by the addition of a 'shortstopping' agent, which may be introduced at various points along the displacement reactor. The conversion normally varies between 60% and 70%, and is controlled by t location at which the shortstop is added and by small variations in the t erature of the last few reactors. Viscosity measurements indicate the nt of reaction. Reactor residence time depends on the particular f ation or 'recipe' being used, but it usually ranges between six and rs.

The latex emerging from the displacement reac eated and then pressured into a series of two flash tanks, operati out 3 PSIG in the first and 4 PSIA in the second, where butadiene and 'ight ends' are taken overhead. The butadiene vapors are compressed, and condensed, and recycled back to the reactor section via recycle st tanks. Non-condensibles are vented to the atmosphere thru the butad absorber tower. The liquid from the second flash tank, partially strippe x, is pumped to the top of a steam stripping tower. The latex flows hru the stripping tower and is pumped out of that tower to the coagulation and drying section. Live steam flows counter-current to the latex (in the tower) and vaporizes the contained styrene. Styrene vapors, steam, small amounts of butadiene and entrained particles of latex are taken overhead. The vapors are condensed, the hydrocarbon and water are separated, and the styrene is recycled to the process.

The stripped latex is coagulated by the addition of salt, followed by acid addition. If the SBR is to be masterbatched, extended by the addition of carbon black and/or oil, either or both of the additives are mixed in with the latex and co-currently coagulated. The coagulation is effected by adding brine to the latex, this partially flocculates or agglomerates the rubber particles and changes the latex consistency from a mobile liquid to a heavy cream. The coagulation is completed by the addition of dilute acid, which converts the layer of soap molecules on the surface of each particle to a fatty acid. This 'breaks' the emulsion and the SBR globules agglomerate to form 'crumbs' of rubber.

The crumbs are washed to remove soluble impurities and dewatered on a screw-type water expeller or a rotary vacuum filter. The dewatered crumbs are broken up in a hammer mill and the SBR particles are blown into the top of a hot air, conveyor type dryer. The dried crumb rubber is compacted into 75 pound bales, dusted with talc and packaged in kraft paper bags.

III. Plant Emissions

This section of the survey report is based primarily on information provided by respondents 29-1, 29-2, 29-4, and 29-5.

A. Continuous Air Emissions

1. Butadiene absorber Vent

Following polymerization, unreacted butadiene is flashed off, compressed, condensed, and recycled. The non-condensible contaminants - mostly air - are vented to atmosphere through an absorption column. Small amounts of butadiene (about .0001 lbs. butadiene/lb. of SBR) are vented along with the non-condensibles. The pertinent data are summarized in Table III.

2. Carbon Black Operations

Most styrene-butadiene rubbers are 'extended' by the addition of oil and/or carbon black, which simultaneously imparts various desirable characteristics to the rubber, and decrease the per pound cost of the finished product. These two components constitute an average of 40 wt. % of extended rubbers. If the oil or carbon black is added to the SBR latex prior to coagulation (see flow diagram) the operation is called masterbatching. More than two thirds of all styrene butadiene rubbers are masterbatched. The handling of carbon black during masterbatching results in the emission of carbon black particles to the air. Three respondents have reported these emissions and it may be assumed that all operators involved in carbon black masterbatching generate similar emissions. Based on three replie these emissions amount to about .001 lbs. of carbon black/lb. of SBR.

3. Dryer Vent

The predominant method for drying the dewatered SBR crumbs is in a perforated apron type, hot air, continuous dryer. Dryer residence time is about two hours. The crumbs may contain up to 30 percent moisture prior to drying. The dried crumbs will contain less than 0.50 percent volatile matter. The exhaust gases from the dryer contain water, styrene, and fine particles of SBR. A comparison of the reported composition of this stream is shown below:

Respondent	SBR	Styrene	Water
29-1 ("A" train)		.00058	.08461
29-1 ("B" train)		.00058	.08461
29-2 (Conveyor dryer)	.00002		.05692
29-2 (Extruder dryer)	.00002		.01897
29-3*	.00001 to .00009	.0007 to .00018**	.021 to .038

---

*Composition range of various unspecified streams that have tentatively been identified as drier vent streams

**Identified only as hydrocarbons.

In addition to the components tabulated above, there are other emissions associated with the operation of the dryer. Operator 29-4 reports that his dryers are gas fired, burning 459.3 MM ft.^{3}/yr. of gas containing .0625 wt. % sulfur. This results in the emission of .00005 lbs. SO_2/lb. of SBR. Presumably some of the other plants utilize direct fired heaters, but none reported emissions from this source.

Extruder driers are also used to dry some types of SBR. In these devices, water and other volatile materials are vaporized, mainly by energy transferred from the screw which forces the rubber through the barrel.

Other techniques, such as the formation of thin sheets of rubber on a paper maker's type of dewatering screen permits short drying times to be utilized. But, whatever the type of drying apparatus, it seems reasonable to assume that most operators will discharge some amount of hydrocarbons to the atmosphere during drying.

4. Engine Exhausts

Respondents 29-1 and 29-6 both indicate that internal combustion engines burning natural gas, are used to drive certain process equipment. Respondent 29-1 reports that his seven engines burn 260 MM ft.^{3}/yr. of gas containing less than 40 grains of sulfur/M ft.^{3}; this represents less than .00001 lbs. of SO_2/lb. of SBR. Data on unburned hydrocarbons, NO_x and CO were not furnished by either respondent.

B. Intermittent Air Emissions

Talc Dusting Operations

The crumb rubber product from the SBR plant is normally formed into 75 lb. bales and packaged in multi-layer paper bags. Talc is applied to the exterior of the bale to prevent the rubber from sticking to the inside of the bag. The dusting is accomplished by air blowing the talc onto the bales as they pass through a 'dust chamber' on a conveyor belt. Respondent 29-1 states that his is an intermittent operation and that 12,000 lbs. a year of talc (.00003 lbs./lb. of SBR) is discharged to the atmosphere. Respondent 29-3 reports an emission of .00001 lbs. of talc/lb. of SBR.

C. Continuous Liquid Wastes

1. Waste Water

The following waste water rates were reported by the respondents:

Plant	Water Rate	Water Treatment
29-1	1,050 GPM	Yes - In plant facilities
29-2	1,330 GPM	Yes - In plant facilities
29-3	1,350 GPM	Yes - In plant facilities
29-4	2,900 GPM	Yes - In plant facilities
29-5	450 GPM	Yes - In plant facilities
29-6	< 1 GPM (?)	Yes - In plant facilities

Several plants report, and probably most plants are similar in this respect, that certain of their waste water stream contain suspended particles of carbon black and rubber. These streams are sent to settling ponds, which are periodically dredged. The 'recovered' sediment is normally disposed of in sanitary land fill areas.

2. Waste Caustic

Butadiene, prior to being charged to the polymerization reactors, is sometimes caustic washed to remove polymerization inhibitors. This results in the generation of some liquid wastes, however, no respondents reported such a waste stream.

D. Intermittent Liquid Wastes

No waste streams in this category were reported.

E. Solid Wastes

Respondents 29-1, 29-2, and 29-3 all report the use of land fill areas for the disposal of solid wastes. The operator of plant 29-4 utilizes the services of a local disposal contractor whereas plants 29-5 and 29-6 report incinerating solid wastes (emissions from the incinerators were not reported).

F. Odors

In general, questionnaire responses seem to indicate that the production of SBR is not a process that has an odor problem.

No respondent reported any odor complaints in the past year. Most, however, did report that odors are occasionally detectable at the plant site. Although the odoriferous materials were not identified, the odor itself is described as the "typical rubber plant smell". This odor is most commonly associated with the rubber drying operation. Lack of community complaints implies that odor control is currently adequate.

G. Fugitive Emissions

Only operator 29-1 has offered an estimate of fugitive emissions. If it is assumed that this estimate is both (1) reasonably accurate and (2) typical of the industry as a whole, then one must conclude that fugitive emissions account for about half of all the atmospheric pollutants released as a result of the production of SBR via emulsion polymerization. Operator 29-1's estimate of fugitve emissions is:

	Component - Lb./Lb. of SBR		
Plant Area	Stryene	Butadiene	Ammonia
Reactor Section	.00004	.00034	.00030
Monomer Recovery	<.00001	.00034	
Tank Farm	.00004	.00017	
Compressor House			.00046
Total	.00008	.00085	.00076

H. Other Sources

A very large number of chemicals with potential for producing air and water pollution are utilized in varying amounts by SBR producers. These include nitrogen and sulfur containing compounds, metallic salts, numerous organics and several powder-form solids. Fortunately, the potential is, for the most part, unrealized and these compounds are 'locked-up' in the SBR polymer without being emitted. All reported emissions are summarized in Table III - National Emissions Inventory.

IV. Emission Control

The few emission control devices that were reported as being employed, by respondents to the questionnaire pertaining to the subject process, are summarily described in Table IV of this report. An efficiency has been assigned each device when data sufficient to calculate it have been available. Three types of efficiency are normally calculated:

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{lbs. of specific pollutants in} - \text{lbs. of specific pollutant out}}{\text{lbs. of specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR}^* = \frac{\Sigma(\text{lbs. of pollutant x wf) in} - \Sigma(\text{lbs. of pollutant x wf) out}}{\Sigma(\text{lbs. of pollutant x wf) in}} \times 100$$

*where wf = weighting factor designated in Table SB VII of this report.

Usually a combustion type control device (i.e., incinerator, flare, etc.) will be assigned both a "CCR" and a "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V of this report.

Since data sufficient to permit device efficiency calculation are available for only three of the fourteen devices summarized in Table IV (Catalog of Emission Control Devices), a few general comments regarding device performance are in order:

Absorbers

Most respondents chose to classify their butadiene absorbers as air pollution control devices. They do minimize air pollution but that is not their primary function. (See Section II)

Of the five absorbers reported, data sufficient to calculate efficiencies were available on only two, SB-6 and SB-9; their efficiencies were reported as 96.5% and 98% respectively.

However, a comparison of the economic data pertaining to these two devices (in Table SB-IV) discloses some inconsistencies. This results from the fact that the operator of device SB-6 is crediting recovered butadiene at 2-3¢/lb. whereas the operator of device SB-9 is crediting it at 10-11¢/lb. (The current selling price of pure butadiene is 10-11¢/lb.)

Absorbers were not employed as pollution abatement devices elsewhere in the respondents' SBR plants.

Scrubbers

Four respondents reported using scrubbers to control pollution, the devices used are listed in Table SB-IV as SB-5, 7, 10, and 12. All are employed to minimize the emission of carbon black particles. All use water as the scrubbing liquid. Devices SB-7 and SB-10 are identified as spray type scrubbers while 29-6 is designated as a 'high energy' scrubber. Only one respondent provides sufficient data for the calculation of scrubber efficiency; device SB-10 has a calculated efficiency of 95%. Respondent 29-3 reports visible emissions from device SB-7. Because of the extremely small size of the carbon black used by the rubber industry, (grades HAF, SAF, ISAF, etc., with average size around 0.2 microns), high energy type scrubbers are required for high recovery efficiencies. Venturi and flooded disc scrubbers would probably be quite effective and should give efficiencies in the 99+ range.

Cyclones

The two cyclones (SB-2 and SB-13) listed in Table SB-IV are both used to minimize talc losses from the bale dusting operation. Data sufficient to calculate the efficiencies of these devices were not reported. Device SB-2 is described as a 'Dustex Microclone' and was installed when the government owned the plant. Device SB-13 is a single stage device, but is 'backed-up' by a bag filter...so it's efficiency is not critical. Standard low resistance cyclones, as these two devices are though to be, could be expected to recover particles in the size range associated with talc (1 to 20 microns) at an efficiency no higher than about 75%.

Bag Filters

Two bag filters are reported by the respondent. device SB-4 and SB-14 (SB-13 listed under cyclones, see note IV, Table IV). No collection efficiencies are indicated, but the device in the more difficult carbon black service (SB-4) should be capable of 99+ %, as indicated by an extensive study of devices in this particular service. (See Report Number EPA-450/3-006a)

Incineration Devices

Two flares are listed in Table IV, they are identified therein as devices SB-8 and SB-14. Unfortunately, none of the (3) respondents supplying information about these two flares provided any description of their location or exactly what they are burning. Most probably they are 'plant flares' and are used to burn materials from pressure relief valves, emergency vents, etc. Due to the great variety of raw materials used in the production of SBR (respondent 29-5 lists 39 different raw materials), the composition of the material being burned by the flare could vary considerably. Flare efficiency would vary accordingly, probably being greater than 90% CCR for 'straight' hydrocarbons, with a proportionately lower SERR for compounds containing nitrogen, sulfur, metals, etc.

Changes in operating conditions, or more specifically changes in emulsion polymerization conditions, would have a negligible effect on atmospheric emissions. The emissions from the process result primarily from fugitive losses, masterbatching, talcing operations and monomer recovery; and thus will not be directly affected by such changes.

Changes in polymerization techniques, such as a change from emulsion polymerization to solvent polymerization, could have an affect on overall emissions. For example, solvent polymerization could result in increased emissions due to solvent losses (see Table SB-III, plant 29-4, "Dryer Exhaust" - of .006 lbs. of hexane emission/lb. of SBR, which are losses from a solvent polymerization train). However, a lack of questionnaire based data on this subject probably places it outside the scope of this particular survey report. To include it would involve mailing additional questionnaires to operators of non-emulsion type SBR plants.

Developmental work (some of which has either been tried or is in progress) directed toward reducing emissions from this process might be directed along the following lines:

(1) Devise technique, whereby no monomer is recycled, that is, where polymerization is complete. This would do away with butadiene absorber and associated emissions, although earlier work has resulted in lower quality rubber when striving for higher conversions.

(2) Devise method for recycling dryer exhaust gases.

(3) Develop non-polluting substitute for talcing operation.

(4) Utilization of best available technology in carbon black recovery operations.

(5) Develop substitute method of handling coagulated latex, one where small crumbs or SBR fines are not generated and subseuqently emitted to the atmosphere during drying and packaging operations. Extruder driers have resulted in some progress in this direction.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken. The reported emission data indicate that the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emissions of pollutants from these new plants. It should be noted that the low predicted growth rate of the industry is responsible, in part, for the very low SEI. Additionally, it is assumed that all new plants will employ emulsion polymerization. This is most probably a false assumption, however, since the SEI is so low, it is very doubtful that the utilization of other polymerization techniques in the new plants could increase the SEI to the extent that the industry would be considered other than a low polluter.

The Table V forecast of 1980 U.S. capacity is based on a 1971 capacity of 1,954 MM long tons/yr. and a growth rate of 2%/year. The predicted growth rate is an average of the various growth rates that have appeared in the literature. The July 12th, 1971 issue of Oil Plant & Drug Reporter (now Chemical Marketing) predicts a 1%/year growth rate, whereas other sources predict up to 3%/year.

On a weighted emission basis a Significant Emission Index of 170 has been calculated in Table VII. This is substantially lower than the anticipated SEI's of other processes in the study. Hence, the recommendation to exclude an in-depth study of the subject process from the overall scope of work for this project

VI. Styrene Butadiene Rubber Producers (Domestic)

Producer	Capacity (1)
American Synthetic Rubber	125,000
B. F. Goodrich	193,000
Ashland	60,000
Copolymer	125,000
Firestone	360,000
General Tire	110,000
Goodyear	403,000
Phillips	77,000
Polymer Corporation	50,000
Shell	116,000
Standard Brands	40,000
Texas - U. S.	148,000
Uniroyal	28,000
Other (2)	119,000
	1,954,000 (3)

NOTES:

(1) Long tons of net polymer. (1971 capacity)

(2) Eight producers with annual capacity of 20,000 tons or less.

(3) Includes 407,000 tons of latex.

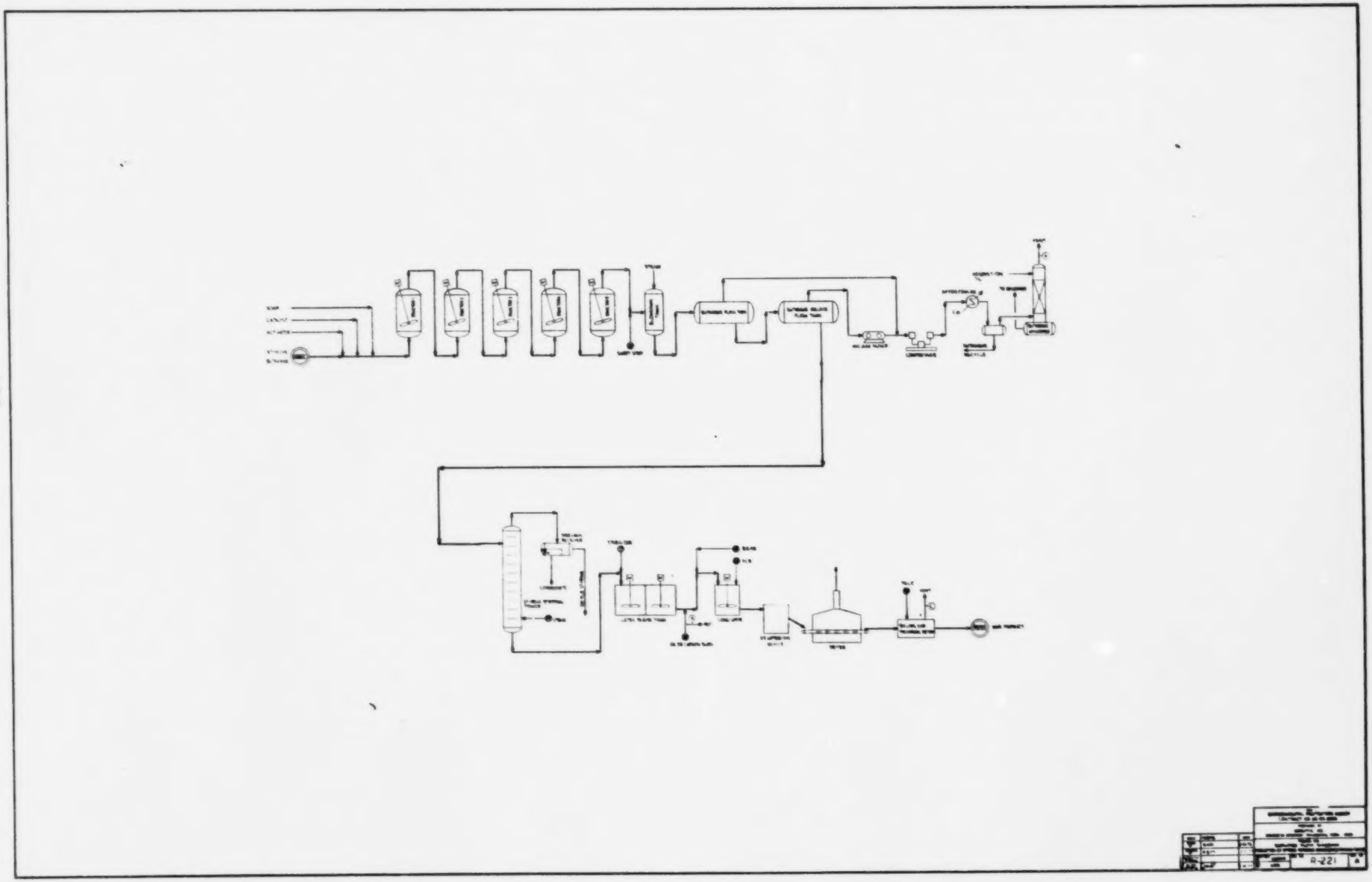
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TABLE SB-I-A
TYPICAL STYRENE BUTADIENE RUBBER RECIPES

The following recipes are typical of the formulations used in the production of cold (41° F) rubber. (Hot SBR now constitutes only a minor portion of total SBR production.)

Peroxamine Recipe

This type formulation is used when rosin soap is to be avoided, in which case potassium fatty acid soap is used as the emulsifier and 'peroxamine' as the activator.

Component	Parts by Weight
Water	200
Butadiene	72
Styrene	28
Potassium fatty acid soap	4.7
Trisodium phosphate - 12 H_2O	0.8
Tamol N	0.15
Diethylene triamine	0.15
P-menthane hydroperoxide	0.12
Ferrous sulfate - 7 H_2O	0.002
Versene Fe-3	0.02
Tert-dodecyl mercaptan	0.02

Sulfoxylate Recipe

This type formulation has the advantage of (1) easily prepared activators, (2) non-slurry activator, (3) uniform polymerization rates (4) 'revivable' polymerization and (5) relatively low cost components.

Component	Parts by Weight
Water	200
Butadiene	70
Styrene	30
Potassium soap of disproportionated rosin	4.5
Trisodium phosphate - 12 H_2O	0.8
Tamol N	0.15
Sodium formaldehyde sulfoxylate - 2 H_2O	0.15
Ferrous sulfate - 7 H_2O	0.05
Versene Fe-3	0.07
P-menthane hydroperoxide	0.10
Tert-dodecyl mercaptan	0.20

TABLE SB-I-B
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

APPROXIMATE GROSS HEAT BALANCE
POLYMERIZATION REACTOR SECTION ONLY

HEAT OUT	TOTAL SYSTEM BTU/LB. OF SBR PRODUCED (1)
Cool feed from ambient to polymerization temperature (75° to 41° F)	82
Maintain reactants at temperature	217
Total Heat Out (3) (4)	299
HEAT IN	
Heat of polymerization (2)	217
Steam-heat latex and unreacted monomers (to 75° for purpose of heat balance)	82
Total Heat In (3) (4)	299

(1) Polymer only - does not include carbon black and oil (which if considered would lower reactor heat req'ts./lb. of extended rubber).

(2) Based on 60% conversion. (Actual heat is about 500 BTU/lb. polymerized.)

(3) Does not account for energy input of agitators.

(4) Assumes no butadiene condensation or vaporization.

TABLE SB-II
LIST OF ORIGINAL GOVERNMENT OWNED SBR PLANTS AND PERTINENT DATA

Name of Company	Location of Plant	Rated Capacity, Long Tons per Year	Date Construction Started	Date Operation Started	Estimated Plant Investment $	Production* 1945
Firestone Tire & Rubber Co.	Akron, Ohio	15,000 15,000	7-28-41	4-26-42 1-21-43	7,300,000	30,976
Firestone Tire & Rubber Co.	Lake Charles, La.	30,000 30,000	9-14-42	9- 1-43 4-19-44	14,000,000	66,306
Firestone Tire & Rubber Co.	Port Neches, Texas	30,000 30,000	6- 4-42	11-28-43 3-15-44	16,400,000	63,505
B. F. Goodrich Co.	Louisville, Ky.	22,500 22,500 15,000	2-15-42	11-27-42 2-19-43 6- 4-43	11,200,000	62,213
B. F. Goodrich Co.	Borger, Texas	30,000 15,000	9-15-42	7-27-43 11-18-43	8,900,000	48,524
B. F. Goodrich Co.	Port Neches, Texas	30,000 30,000	6- 4-42	8-22-43 3- 3-44	16,400,000	63,430
Goodyear Synthetic Rubber Corp.	Akron, Ohio	15,000 15,000	6- 1-41	5-18-42 6- 8-43	8,400,000	29,697
Goodyear Synthetic Rubber Corp.	Houston, Texas	30,000 30,000	8- 8-42	10-26-43 4- 9-44	13,500,000	63,997
Goodyear Synthetic Rubber Corp.	Los Angeles, Calif.	30,000 30,000	9- 1-42	6-15-43 10-25-43	11,340,000	29,730
U. S. Rubber Co.	Naugatuck, Conn.	10,000 20,000	9-31-41	9- 4-42	9,000,000	30,357
U. S. Rubber Co.	Institute, W. Va.	30,000 30,000 30,000	6-18-52	3-31-43 7-28-43 9-15-43	18,750,000	97,845
U. S. Rubber Co.	Los Angeles, Calif.	30,000	9- 1-42	10-13-43	5,670,000	33,805
Copolymer Corp.**	Baton Rouge, La.	30,000	10-29-42	3-31-43	7,850,000	32,849
General Tire & Rubber Co.***	Baytown, Texas	30,000	9-24-42	7-21-43	8,000,000	32,660
National Synthetic Rubber Corp.****	Louisville, Ky.	30,000	12-15-42	9-30-43	7,630,000	31,794
					164,340,000	717,688

*Excludes materials blended into the latex.

**Operated by Copolymer Corp. comprised of: Armstrong Rubber Co., West Haven, Conn.; Dayton Rubber Manufacturing Co., Dayton, Ohio; Gates Rubber Co., Denver, Colo.; Lake Shore Tire & Rubber Co., Des Moines, Ia.; Sears, Roebuck & Co., Chicago, Ill. (including Armstrong Tire & Rubber Co., Natchez, Miss., in which Sears, Roebuck & Co. owns 50 per cent of the voting stock); Mansfield Tire & Rubber Co., Mansfield, Ohio; Pennsylvania Rubber Co., Jeannette, Pa.

***Operated by General Tire & Rubber Co. (General Latex & Chemical Co., Cambridge, Mass. Associates)

****Operated by National Synthetic Rubber Corp. comprised of: Goodall Rubber Co., Trenton, N. J.; Hewitt Rubber Co., Buffalo, N. Y.; Lee Rubber & Tire Co., Conshohocken, Pa.; Minnesota Mining & Manufacturing Co., St. Paul, Minn. (including Inland Rubber Corp., a subsidiary)

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Page 1 of 8

Plant EPA Code No.	29-1			
Capacity, Tons of SBR/Yr.	219,000			
Range in Production - % of Max.	5.7			
Emissions to Atmosphere				
Stream	Reactor - Train "A" Fugitive Emissions	Train "A" Recovery Area Fugitive Emissions	Butadiene - "A" Absorber Vent	Train "A" Dryer
Flow - Lbs./Hr.	17	9	1	4,260
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent Hrs./Yr. - Flow				
Composition, Tons/Ton of SBR				
Styrene	.00002	∠.00001		.00058
Butadiene	.00017	.00017	.00001	
Ammonia	.00015			
Water				.08461
Talc				
Carbon Black				
Butene				
Hexane				
Methane				
Oxygen				
Nitrogen				
SBR				
NO_x				
SO_x				
Misc. HC				
CO				
CO_2				
Vent Stacks	No	No	Not given	Yes
Number				8
Height - Ft. (above grade)				(44)
Diameter - Inches				4 @ 30, 4 @ 36
Exit Gas Temp. - F°				170
SCFM/Stack				~1000
Emission Control Devices	No	No	Yes, SB-1	No
Absorber/Scrubber			+	
Cyclones				
Bag Filer				
Flare				
Analysis	None	None		None
Date or Frequency of Sampling			Bi-daily	Never
Sample Tap Location			Absorber	None
Type of Analysis	Calc'd.	Calc'd.	GLC	Estimate
Odor Problem	No	No	No	No

Summary of Air Pollutants
Hydrocarbons, Ton/Ton of SBR
Particulates, Ton/Ton of SBR
NO_x, Ton/Ton of SBR
SO_x, Ton/Ton of SBR
CO, Ton/Ton of SBR

SEE CONTINUATION

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Page 2 of 8

Plant EPA Code No.	24-1			
Capacity, Tons of SBR/Yr.	214,000			
Range in Production - % of Max.	5.7			
Emissions to Atmosphere				
Stream	Train "A" Talc Dust	Reactor Train B Fugitive Emissions	Train "B" Recovery Area Fugitive Emissions	Butadiene "B" Absorber Vent
Flow - Lbs./Hr.	12,000/Yr.	17	9	1
Flow Characteristic, Continuous or Intermittent	Intermittent	Continuous	Continuous	Continuous
if Intermittent, Hrs./Yr. - Flow	Not specified			
Composition, Tons/Ton of SBR				
Styrene		.00002	<.00001	
Butadiene		.00017	.00017	.00001
Ammonia		.00015		
Water				
Talc	.00003			
Carbon Black				
Butene				
Hexane				
Methane				
Oxygen				
Nitrogen				
SBR				
NO_x				
SO_x				
Misc. HC				
CO				
CO_2				
Vent Stacks		No	No	Not given
Number				
Height - Ft. (above grade)				
Diameter - Inches				
Exit Gas Temp. - F°				
SCFM/Stack				
Emission Control Devices	Yes, SB-2	No	No	Yes, SB-3
Absorber/Scrubber				+
Cyclones	+			
Bag Filter				
Flare				
Analysis	None	None	None	
Date or Frequency of Sampling	Never			Bi-daily
Sample Tap Location	None			Absorber
Type of Analysis	Estimate	Calc'd.	Calc'd.	GLC
Odor Problem	No	No	No	No
Summary of Air Pollutants				
Hydrocarbons, Ton/Ton of SBR		SEE CONTINUATION		
Particulates, Ton/Ton of SBR				
NO_x, Ton/Ton of SBR				
SO_x, Ton/Ton of SBR				
CO, Ton/Ton of SBR				

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TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Plant EPA Code No.	29-1					
Capacity, Tons of SBR/Yr.	219,000					
Range in Production - % of Max	5.7					
Emissions to Atmosphere						
Stream	Train B Dryer	Carbon Black ex Bag Filter	Carbon Black ex Scrubber	Carbon Black Section Fugitive Emissions	Tank Farm Fugitive Emissions	Compressor House Fugitive Emissions
Flow - Lbs./Hr.	4,260	2	1	1	11	23
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent Hrs./Yr. - Flow						
Composition, Tons/Ton of SBR						
Styrene	.00058				.00004	
Butadiene					.00017	
Ammonia						.00046
Water	.08461					
Talc						
Carbon Black		.00004	.00001	.00003		
Butene						
Hexane						
Methane						
Oxygen						
Nitrogen						
SBR						
NO_x						
SO_x						
Misc. HC						
CO						
CO_2						
Vent Stacks	Yes	Not specified	Not specified	No	No	No
Number	8					
Height - Ft. (above grade)	(44)					
Diameter - Inches	4 @ 30, 4 @ 36					
Exit Gas Temp. - F°	170					
SCFM/Stack	~1000					
Emission Control Devices	No	Yes, SB-4	Yes, SB-5	No	No	No
Absorber/Scrubber			+			
Cyclones						
Bag Filter		+				
Flare						
Analysis	None	None	None	None	None	None
Date or Frequency of Sampling	Never					
Sample Tap Location	None					
Type of Analysis	Estimate	Estimate	Estimate	Estimate	Estimate	Estimate
Odor Problem	No	No	No	No	No	No
Summary of Air Pollutants						
Hydrocarbons, Ton/Ton of SBR				.00213		
Particulates, Ton/Ton of SBR				.00087		
NO_x, Ton/Ton of SBR				0		
SO_x, Ton/Ton of SBR				0		
CO, Ton/Ton of SBR				0		

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

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Plant EPA Code No.		29-2	
Capacity, Tons of SBR/Yr.		112,000	
Range in Production - % of Max.		0	
Emissions to Atmosphere			
Stream	Butadiene Absorber Vent	Conveyor Drier Vent	Extruder Drier Vent
Flow - Lbs./Hr.	62	135,744	90,850
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous
If Intermittent, Hrs./Yr. - Flow			
Composition, Tons/Ton of SBR			
Styrene			
Butadiene	.00017		
Ammonia			
Water		.05692	.01897
Talc			
Carbon Black			
Butene	.00006		
Hexane			
Methane	.00002		
Oxygen	.00043	1.03714	.70154
Nitrogen	.00140	3.43077	2.30784
SBR		.00002	.00002
NO_x			
SO_x			
Misc. HC			
CO			
CO_2			
Vent Stacks	Yes	Yes	Yes
Number	1	6	2
Height - Ft. (above grade)	(40)	(40)	(30)
Diameter - Inches	1	30 - 36	24
Exit Gas Temp. - F°	70	170	220
SCFM/Stack	13	~5,000	10,000
Emission Control Devices	Yes, SB-6	No	None
Absorber/Scrubber	+		
Cyclones			
Bag Filter			
Flare			
Analysis	Yes	None	None
Date or Frequency of Sampling	Not specified	None	None
Sample Tap Location	Absorber Overhead		
Type of Analysis	GLC	Calc'd.	Calc'd.
Odor Problem	No	No	No
Summary of Air Pollutants			
Hydrocarbons, Ton/Ton of SBR		.00023	
Particulates, Ton/Ton of SBR		.00004	
NO_x, Ton/Ton of SBR			
SO_x, Ton/Ton of SBR			
CO, Ton/Ton of SBR			

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

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Plant EPA Code No. 29-3
Capacity, Tons of SBR/Yr 175,000
Range in Production - % of Max 0

Emissions to Atmosphere Stream	Carbon Black Section Vent (I)	Emission "C" (I)	Emission "D" (I)	Emission "E" (I)	Emission "F" (I)
Flow - Lbs./Hr.	715	Not specified	Not specified	Not specified	Not specified
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent, Hrs./Yr. - Flow					
Composition, Tons/Ton SBR					
Styrene					
Butadiene					
Ammonia					
Water	.01779		02988	07076	.05763
Talc					
Carbon Black	.00010		.00001	<.00001	<.00001
Butene					
Hexane					
Methane					
Oxygen	+				
Nitrogen	+				
SBR			+	+	+
NO_x		+			
SO_x		+			
Misc. HC		+	.00008	.00008	.00006
CO		+			
CO_2					
Vent Stacks		Yes	Yes	Yes	Yes
Number	1	1	1	1	1
Height - Ft. (above grade)	40	30	40	41.5	41.8
Diameter - Inches	6	20	34	34	34
Exit Gas Temp. - F°	165	470	147	154	152
SCFM/Stack	300	345	8,890	11,700	10,800
Emission Control Devices	Yes, SB-7	No	No	No	No
Absorber/Scrubber	+				
Cyclones					
Bag Filter					
Flare					
Analysis		None			
Date or Frequency of Sampling	Once		Once	Once	Once
Sample Tap Location	Stack				
Type of Analysis	Estimate	Calc'd.	Calc'd.	Calc'd.	Calc'd.
Odor Problem	No	No	No	No	No
Summary of Air Pollutants					
Hydrocarbons, Ton/Ton of SBR					
Particulates, Ton/Ton of SBR					
NO_x, Ton/Ton of SBR			SEE CONTINUATION		
SO_x, Ton/Ton of SBR					
CO, Ton/Ton of SBR					

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Plant EPA Code No.	29-3
Capacity, Tons of SBR/Yr.	175,000
Range in Production - % of Max.	0

Emissions to Atmosphere					
Stream	Emission "G" (I)	Emission "H" (I)	Emission "I" (I)	Emission "J" (I)	Emission "K" (I)
Flow - Lbs./Hr.	Not specified	Not specified	Not specified	Not specified	Not specified
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent, Hrs./Yr. - Flow					
Composition, Tons/Ton SBR					
Styrene					
Butadiene					
Ammonia					
Water	.06030	.03486	.03785	.03812	.03760
Talc					
Carbon Black	<.00001				
Butene					
Hexane					
Methane					
Oxygen					
Nitrogen					
SBR	+	<.00001	.00001	<.00001	<.00001
NO_x					
SO_x					
Misc. HC	.00006	.00018	.00018	.00015	.00015
CO					
CO_2					
Vent Stacks	Yes	Yes	Yes	Yes	Yes
Number	1	1	1	1	1
Height - Ft. (above grade)	40	416	40.8	40.8	40.3
Diameter - Inches	34	34	34	34	34
Exit Gas Temp. - F°	155	154	154	153	145
SCFM/Stack	11,300	14,000	14,000	14,100	15,100
Emission Control Devices	No	No	No	No	No
Absorber/Scrubber					
Cyclones					
Bag Filter					
Flare					
Analysis					
Date or Frequency of Sampling	Once	Once	Once	Once	Once
Sample Tap Location					
Type of Analysis	Calc'd.	Calc'd.	Calc'd.	Calc'd.	Calc'd.
Odor Problem	No	No	No	No	No
Summary of Air Pollutants					
Hydrocarbons, Ton/Ton of SBR					
Particulates, Ton/Ton of SBR					
NO_x, Ton/Ton of SBR					
SO_x, Ton/Ton of SBR					
CO, Ton/Ton of SBR					

SEE CONTINUATION

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Plant EPA Code No.			29-3		
Capacity, Tons of SBR/Yr.			175,000		
Range in Production - % of Max			0		
Emissions to Atmosphere					
Stream	Emission "L" (I)	Emission "M" (I)		Emission "N" (I)	**Flare** Flue Gas
Flow - Lbs./Hr.	Not Specified	Not Specified		Not Specified	Not Specified
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous		Continuous	Continuous
If Intermittent, Hrs./Yr. - Flow					
Composition, Tons/Ton SBR					
Styrene					
Butadiene					
Ammonia					
Water	.02094	.03442			+
Talc				.00001	
Carbon Black					
Butene					
Hexane					
Methane					
Oxygen					
Nitrogen					
SBR	.00001	.00009			
NO_x					
SO_x					
Misc. HC	.00010	.00007			
CO					
CO_2					+
Vent Stacks	Yes	Yes		Yes	Yes
Number	1	1		1	1
Height - Ft. (above grade)	45.3	45.5		30	150
Diameter - Inches	24	18		6	18
Exit Gas Temp. - F°	165	102		90	280
SCFM/Stack	10,900	6,720		800	500
Emission Control Devices	No	No		No	Yes SB-8
Absorber/Scrubber					
Cyclones					
Bag Filter					
Flare					+
Analysis					
Date or Frequency of Sampling	Once	Thrice		Never	Never
Sample Tap Location					
Type of Analysis	Calc'd	Calc'd.		Calc'd	Calc'd.
Odor Problem	No	No		No	No
Summary of Air Pollutants					
Hydrocarbons, Ton/Ton of SBR			.00111		
Particulates, Ton/Ton of SBR			.00029		
NO_x, Ton/Ton of SBR			+		
SO_x, Ton/Ton of SBR			+		
CO , Ton/Ton of SBR			+		

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Page 8 of 8

Plant EPA Code No.	29-4				29-5		29-6
Capacity, Tons of SBR/Yr	342,000				109,000		360,000
Range in Production - % of Max	0				0		0
Emissions to Atmosphere							
Stream	Butadiene Absorber Vent	Carbon Black Section Vent	Boiler Flue Gas	Dryer Exhaust (II)	Butadiene Absorber Vent	Waste Solids Incinerator Flue Gas	No information given
Flow - Lbs./Hr.	<10	<600		Not specified	13	Not specified	
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Intermittent	
If Intermittent, Hrs./Yr. - Flow							
Composition, Tons/Ton SBR							
Styrene							
Butadiene	.00002				.00007		
Ammonia							
Water		+		+			
Talc							
Carbon Black		.00001				<.00001 (partic.)	
Butene							
Hexane				.00600			
Methane							
Oxygen		+		+	.00039		
Nitrogen		+		+	.00011		
SBR							
NO_x						.00030	
SO_x			.00026				
Misc. HC						.00002	
CO						.00003	
CO_2				+			
Vent Stacks	Yes		Yes	Yes	Yes	Yes	
Number	1	1	6	47	1	1	
Height - Ft. (above grade)	10	Horiz. Disch.	41 to 189	(34) avg.	28	3	
Diameter - Inches	1	4	30 to 108	(30) avg			
Exit Gas Temp. - F°	100	100		150	50		
SCFM/Stack	2	139			2.6		
Emission Control Devices	Yes, SB-9	Yes, SB-10	No	No	Yes SB-11 (III)	No	Yes
Absorber/Scrubber	+	+					+ SB-12
Cyclones							+ } SB-13
Bag Filter							+
Flare							+ SB-14
Analysis	Yes	Yes	No	No	Yes	No	
Date or Frequency of Sampling	Weekly	Once	Never	Never	Daily		
Sample Tap Location	Absorber						
Type of Analysis	GLC	Creimetric	Not specified	Calc'd.	GLC	T.A.C.B. Est.	
Odor Problem	No	No	No	No	No	No	
Summary of Air Pollutants							
Hydrocarbons, Ton/Ton of SBR	.00602				.00009		Can not be determined
Particulates, Ton/Ton of SBR	.00001				<.00001		
NO_x, Ton/Ton of SBR	0				.00030		
SO_x, Ton/Ton of SBR	.00026						
CO , Ton/Ton of SBR	0				.00003		

TABLE SB-III
NATIONAL EMISSIONS INVENTORY
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

EXPLANATION OF NOTES

I. Respondent reported emissions during period of low plant thru-put (25 - 50% of design), normally-when appropriate-emissions are adjusted as follows:

$$\text{actual emissions} = \frac{\text{reported emissions} \times 100}{\text{reported plant thru-put as \% of design}}$$

However, after comparing reported emissions with data from other respondents, no adjustment was made.

II. This emission results from solution polymerization unit, which respondent operates in tandem with emulsion process.

III. Respondent did not claim device SB-11 as pollution control device, however, as all other respondents did, device was listed here and in Table IV for purposes of comparison.

TABLE SB-IV
CATALOG OF EMISSION CONTROL DEVICES
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Page 1 of 3

	Monomer Recovery Section					Carbon Black Section		
ABSORBERS/SCRUBBERS								
EPA Code No. for plant using	29-1	29-1	29-2	29-4	29-5	29-1	29-3	29-4
Flow Diagram (Fig. 1) Stream I. D.	A	A	A	A	A	B	B	B
Device I. D. No.	SB-1	SB-3	SB-6	SB-9	SB-11	SB-5	SB-7 (II)	SB-10
Controls emission of	Butadiene	Butadiene	Butadiene	Butadiene	Butadiene	Carbon Black	Carbon Black	Carbon Black
Scrubbing/Absorbing Liquid	Absorption Oil	Absorption Oil	Absorption Oil	Absorption Oil	Not Specified	Water	Water	Water
Type - Spray	Not Specified	Not Specified					X	X (Horiz.)
Packed Column			X	X				
Column w/trays								
Number of trays								
Type of tray								
Other						+ Ducon Centrif.		
Scrubbing/Absorbing Liquid Rate - GPM			10				30	
Design Temp. (Operating Temp.) °F			(70°)				160	90
Gas Rate, SCFM (Lb./Hr.)			75	8			360	
T-T Height, Ft.				12			3.25	
Diameter, Ft.				1.25			1.0	
Vented Gases to Stack			Yes	Yes				
Stack Height - Ft.			40					
Stack Diameter - In.			1					
Installed Cost - Mat'l. & Labor - $			50,000 (Est.)	14,000		13,576 (I)	13,188	2,800
Installed Cost Based on - "year" - dollars			1961	1958		1959	1966 - 1971	1961 - 1971
Installed Cost - ¢/lb. of SBR/Yr.			.0223	.0020		.0031	.0038	.00041
Operating Cost - Annual - $ (1972)			22,000	2,095			18,300	3,000
Value of Recovered Product, $/Yr.			30,000	65,000			0	5,115
Net Operating Cost - Annual - $			-8,000	-62,905			18,300	-2,115
Net Operating Cost - ¢/lb. of SBR			Neg.	Neg.			0052	Neg.
Efficiency - % - SE			96.5	~98				95
Efficiency - % - SERR			96.5	~98				95
CYCLONES								
EPA Code No. for plant using								
Flow Diagram (Fig. 1) Stream I. D.								
Device I. D. No.								
Controls Emission of								
T-T Height - Ft.								
Diameter - Ft.								
No. of Stages								
Installed Cost - Mat'l. & Labor - $								
Installed Cost Based on - "year" - dollars								
Installed Cost - ¢/lb. of SBR/year								
Operating Cost - Annual - (1972)								
Value of Recovered Product - $/Yr.								
Net Operating Cost - Annual - $								
Net Operating Cost - ¢/lb. of SBR								
Efficiency - % - SE								
Efficiency - % - SERR								

TABLE SB-IV
CATALOG OF EMISSION CONTROL DEVICES
STYRENE BUTADIENE RUBBER VIA EMULSION POLYMERIZATION

Page 2 of 3

	Product Packaging		Unspecified Area
ABSORBERS/SCRUBBERS			
EPA Code No. for plant using			29-6
Flow Diagram (Fig. 1) Stream I. D.			A ?
Device I. D. No.			SB-12
Controls emission of			Carbon Black?
Scrubbing/Absorbing Liquid			
Type - Spray			
Packed Column			
Column w/trays			
Number of trays			
Type of tray			
Other			
Scrubbing/Absorbing Liquid Rate - GPM			
Design Temp. (Operating Temp.) F°			
Gas Rate, SCFM (lb./hr.)			
T-T Height, Ft.			
Diameter, Ft.			
Washed Gases to Stack			
Stack Height - Ft.			
Stack Diameter - In.			
Installed Cost - Mat'l. & Labor - $			27,500
Installed Cost Based on - "year" - dollars			1967
Installed Cost - ¢/lb. of SBR/Yr.			.0038
Operating Cost - Annual - $ (1972)			
Value of Recovered Product, $/Yr.			
Net Operating Cost - Annual - $			
Net Operating Cost - ¢/lb. of SBR			
Efficiency - % - SE			
Efficiency - % - SERR			
CYCLONES			
EPA Code No. for plant using	29-1 (III)	29-6 (IV)	
Flow Diagram (Fig. 1) Stream I. D.	C	C	
Device I. D. No.	SB-2	SB-13	
Controls Emission of	Talc	Talc	
T-T Height - Ft.			
Diameter - Ft.			
No. of Stages	Multi Stage Parallel Flow	Single	
Installed Cost - Mat'l. & Labor - $	Not Specified	15,000	
Installed Cost Based on - "year" - dollars		1966	
Installed Cost - ¢/lb. of SBR/year		.0021	
Operating Cost - Annual (1972)			
Value of Recovered Product - $/Yr.			
Net Operating Cost - Annual - $			
Net Operating Cost ¢/lb. of SBR			
Efficiency - % - SE			
Efficiency - % - SERR			

TABLE SB-IV
CATALOG OF EMISSION CONTROL DEVICES
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

Page 3 of 3

	Carbon Black Section	Unspecified Areas		
BAG FILTERS				
EPA Code No. for plant using	29-1			
Flow Diagram (Fig. I) Stream I. D.	A			
Device I. D. No.	SB-4			
Controls Emission of	Carbon Black			
Number of Compartments				
Number of Bags/Compartment				
Bag Cloth Material				
Total Bag Area - Ft^2				
Design (Operating) Temp. - F°				
Design (Operating) Press. - PSIG				
Installed Cost - Mat'l. & Labor - $	(V)			
Installed Cost Based on - "year" - dollars				
Installed Cost - ¢/lb. of SBR/Yr.				
Operating Cost - Annual - $ - (1972)				
Value of Recovered Product - $/Yr.				
Net Operating Cost - $/Yr.				
Net Operating Cost - ¢/lb. of SBR				
Efficiency - % - SE				
Efficiecny - % - SERR				
INCINERATION DEVICES				
EPA Code No. for plant using		29-1 (VI)	29-6	29-3 (VI)
Flow Diagram (Fig. I) Stream I. D.				
Device I. D. No.		SB-8	SB-14	SB-8
Type of Compound Incinerated				
Type of Device - Flare		+	+	+
Incinerator				
Other				
Material Incinerated, SCFM (lb./hr.)				
Auxilliary Fuel Req'd. - Excluding Pilot				
Type				
Rate - BTU/Hr.				
Device or Stack Height - Ft.		150	150	150
Installed Cost - Mat'l. & Labor - $		15,288	40,000 (VII)	15,288
Installed Cost Based on - "year" - dollars		1969 - 1970	1970	1969 - 1970
Installed Cost - ¢/lb. of SBR/Yr.		.0044	.0056	.0044
Operating Cost - Annual - $ (1972)		10,600		10,600
Value of Heat or Power Recovery - $/Yr.		0		0
Net Operating Cost - $/Yr.		10,600		10,600
Net Operating Cost - ¢/lb. of SBR		.0024		.0030
Efficiency - % - CCE				
Efficiency - % - SERR				

TABLE SB-IV
CATALOG OF EMISSION CONTROL DEVICES
STYRENE BUTADIENE RUBBER
VIA
EMULSION POLYMERIZATION

EXPLANATION OF NOTES

I Estimated by Houdry, respondent reported equipment (only) cost of $6,788.

II Device SB-7 consists of four identical units, costs given are total for all units.

III. Device SB-2 consists of two identical units, costs given are total for both units.

IV Device SB-13 consists of a cyclone separator with a bag filter on the atmospheric discharge.

V Unit was acquired at unknown cost, respondent reconditioned it in 1969 at cost of $5,067.

VI Device SB-8 is used jointly by respondents 29-1 and 29-3, costs shown are respondents 50% share of total.

VII Respondent indicates cost is for "flare tip" only.

TABLE SB-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
4,464	112	4,352	3,587	5,231	879	250	3 - 4

NOTE:

(1) All capacities in MM lbs./yr.

(2) Current capacity = M long tons = 1,993.
1980 capacity = " " " = 2,335.

(3) 1980 rates based on assumed 2%/yr. growth rate.

TABLE SB-VI
EMISSION SOURCE SUMMARY
TON/TON OF SBR

	Source						
Emission	Monomer Recovery	Polymer Extrusion and Drying	Carbon Black Handling	Packaging	Fugitive Emissions	Heat and Power Cen.	Total
Hydrocarbon	.00010	.00100			.00100		.00210
Particulates & Aerosols		.00002	.00010	.00002	.00021		.00035
NO_x							0
SO_x						.00020	.00020
CO							0

TABLE SB-VII
WEIGHTED EMISSION RATES

Chemical: Styrene-Butadiene Rubber

Process: Emulsion Polymerization

Increased Capacity by 1980 879 MM lbs./yr.

Pollutant	Emission Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factor	Weighted Emissions MM Lbs./Yr.
Hydrocarbons	.00210	1.85	80	147.7
Particulate & Aerosols	.00035	.31	60	18.5
NO_x	0	0	40	0
SO_x	.00020	.18	20	3.5
CO	0	0	1	0

Significant Emission Index = 169.7

Vinyl Acetate via Acetylene

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I. Introduction

Vinyl acetate is an important petrochemical used to produce polymer. Most of the vinyl acetate manufactured is polymerized into polyvinyl acetate which is used in latexes, emulsion paints, adhesives and various textile coatings or futher processed into polyvinyl alcohol or polyvinvl butyral. About 10% is co-polymerized with vinyl chloride, ethylene and other monomers.

Vinyl acetate is currently produced by three processes. The newer two utilize ethylene, oxygen and acetic acid in a vapor or liquid phase reaction. The oldest process, which presently accounts for 30% of vinyl acetate production, uses acetylene and acetic acid in a vapor phase reaction. Because of the high acetylene raw material costs, little, if any, growth is expected in the acetylene based vinyl acetate industry. Older plants are currently being phased out. Total capacity of acetylene based plants is expected to drop while overall growth of vinyl acetate will be about 10% a year through 1980.

Air emissions arising from vinyl acetate produced using acetylene and acetic acid stem primarily from the venting of light by-products. Other sources are incineration of liquid waste and storage tank vent losses. Since the process is not expected to grow, total emission through 1980 will be insignificant compared to other processes being surveyed.

II. Process Description

Vinyl acetate can be produced by the chemical combination of acetic acid and acetylene. The catalyzed reaction is carried out in the vapor phase

$$C_2H_2 + CH_3COOH \xrightarrow{\text{Zinc Acetate}} CH_3COOCH = CH_2.$$

Glacial acetic acid and recycle acid are blended in a charge vaporizer. Recycle plus fresh acetylene enters the tank through a sparger and pass up through the acid. Typical operating conditions for the vaporizer are 4 to 5 PSIG and 160 to 180° F.

The charge is then preheated first by exchange with the reactor effluent and finally with steam. The reaction takes place in a vertical tubular reactor of stainless steel. Typically, the tubes are 12 feet long with a two inch diameter. The packing is composed of granular activated carbon with a 20 to 30 wt. % zinc acetate catalyst. The reactor operates at 350° F with fresh catalyst and the temperature is gradually increased to 400° F as the catalyst ages. Typical space velocities are 300 to 400 hours^{-1}. Excess heat due to the exothermic heat of reaction is removed by heat transfer in the shell side of the reactor.

Yields are quite good, 92 to 98% based on acetylene and 95 to 99% based on acetic acid. Acetic acid conversion is usually about 80%. The molar ratio of acetylene to acetic acid is usually about 4-5 to one.

The effluent gases are cooled in two stages, first by exchange with feed vapors and finally by exchange with a coolant. A mixture of crude vinyl acetate and unreacted acetic acid is condensed in this step, while non-condensibles, primarily acetylene, pass overhead and recycle to the reactor. In the first column, light ends such as residual acetylene, acetone and acetaldehyde are separated, the acetylene can be separated and returned to the reactor, while other light ends are generally vented to the atmosphere. The bottoms from this column passes to another distillation column where a sharp separation is made between vinyl acetate and acetic acid plus waste. Heavy reaction products are removed from the system in a heavy ends column. The acetic acid recovered from overhead is recycled to the charge vaporizer.

The finished vinyl acetate has a purity of 99.5% or better. The Borden Chemical plant in Geismar, Louisiana, is using a modified process developed jointly with Blaw-Knox. The process is the first to make vinyl acetate directly from raw acetylene produced in a partial oxidation process. The operating costs are said to be about 30% less than for a conventional vinyl acetate process. The key to the lower operating costs is in the purification of raw acetylene and recycle acetylene.

III. Plant Emissions

A. Continuous Air Emissions

1. Light Ends Vent

The emissions from this vent constitute the most important source of air pollution associated with the production of vinyl acetate from acetylene.

The stream consists of acetaldehyde, acetylene, acetone, vinyl acetate and acetic acid. The relative composition of components and flow rate from this vent varies greatly between respondents. Factors influencing the flow are 1) amounts of light by-products produced 2) efficiency of product and recycle gas recovery systems. Total hydrocarbon emissions were .0400 lbs./lb. vinyl acetate in the worst case and .0082 lbs./lb. vinyl acetate in the best case. Plant 13-2 plans in the future to either recover this stream in the system or pipe it to the incinerator.

2. Heavy Ends Column Vent

Only respondent 30-3 reported a vent of this type. Acetic acid vapors are the only noxious emission associated with this stream and its flow rate is sufficiently small so that only .0002 lbs./lb. vinyl acetate are released to the atmosphere.

3. Incineration of Liquid Waste

Plant 30-2 reports that heavy organic wastes removed from the system are burned continuously in an incinerator. The liquid separated from acetic acid in the heavy ends column, contains acetaldehyde, acetic anhydride, crotonaldehyde and polymer. Due to the fact that no nitrogen or sulfur is present in the compounds, combustion to CO_2 and H_2O is almost totally complete.

4. Vinyl Acetate Storage Tank Vents

The quantity of vapors released to the amosphere through tank venting was significant for 30-3, the sole plant to supply detailed information. .00754 lbs. of hydrocarbons per lb. vinyl acetate are continuously vented. Other facilities blanketed the liquid with pads of nitrogen or methane to reduce losses.

5. Acetic Acid Storage Tank Vents

Negligible amounts of acetic acid are vented to the amosphere.

B. Intermittent Air Emissions

1. Incineration of Liquid Waste

Some plants store their heavy organic liquid and burn it for a few hours weekly or monthly. The waste is identical in composition to that described in Section A-3. The quantity of flow varies depending on the system. Organic liquid is either burned in open air or in an atmospheric liquid waste burner. As in the case of the continuous incinerator, combustion is almost totally complete and only small amounts of particulates are produced.

2. Reactor Emergency Vent

In case of a compressor breakdown or system malfunction, vinyl acetate converters are equipped with an emergency blow-off system. Failure is said to occur about five times a year and lasts from one hour to one day. Light hydrocarbons of all types are released to the atmosphere under these conditions.

3. Reactor Purge Gas

Respondent 30-3 reports that approximately ten times a year for a duration of six hours the reactor is purged with acetic acid and nitrogen when preparing for catalyst change. Emissions on a yearly basis are small, .0001 lbs. of acetic acid per lb. vinyl acetate.

C. Continuous Liquid Wastes

1. Heavy Organic Liquid Waste

Residue from the heavy ends column is burned as described above.

2. Waste Water

Plants 30-3 and 30-4 report waste water streams.

Plant	GPH	% Organic	Treatment
30-2	0		
30-3	4,400	10%	Primary
30-4	150	Not Specified	Off-site

D. Intermittent Liquid Waste

No waste streams in this category were reported.

E. Solid Waste

Spent catalyst and residue carbon are removed to land fill.

F. Odors

All respondents reported that acetic acid and acetaldehyde odors were present on plant property but they claim the odor does not carry off plant property. On this basis, it is concluded that the production of vinyl acetate does not present a community odor problem.

G. Fugitive Emissions

No sources of fugitive emissions were mentioned.

IV. Emission Control

The only emission control devices reported as being employed by respondents was liquid waste incinerators whose function can be described as water pollution control. Never-the-less, since their overall purpose is that of reducing harmful pollutants they are summarily described in Table IV. An efficiency has been assigned each device.

(1) CCR - Completeness of Combustion Rating

$$CCR = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

A more complete description of this rating method may be found in Appendix V of this report.

Incineration Methods Employed

1) Incinerator
2) Atmospheric Liquid Waste Burner
3) Open Air Burning

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken for the following reasons:

1. The reported emissions data indicate that the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed.

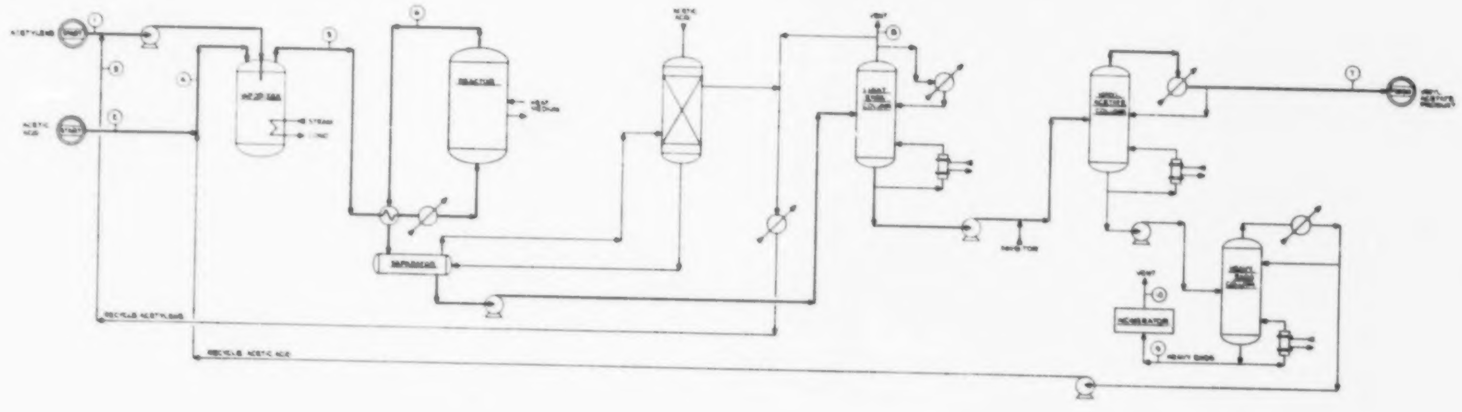
2. Due to the high cost of acetylene, new plants are expected to be built using one of the ethylene processes. Ethylene is presently selling at about 3¢ per pound while acetylene is difficult to obtain at 9¢ per pound. Many companies (USI, Celanese, DuPont) have already built new plants using ethylene as the starting material. Monsanto and several other companies have phased out their acetylene based vinyl acetate production. Union Carbide plans to follow suit by putting its 225 MM lbs/year Texas City plant on a stand-by basis by 1974, due to high acetylene costs and old equipment. Borden Chemical and National Starch and Chemical will be the only acetylene based producers in 1974. Bordern uses the Blaw-Knox acetylene process which is more economical than the older method. One new acetylene type vinyl acetate plant is projected to be built on the possibility that lower acetylene raw material costs and other factors could make such a project economical. The growth forecast is summarized in Table V.

On a weighted basis, a Significant Emission Index of 360 has been calculated in Table VII. The low number is attributed to the fact that little or no growth of this process is expected. Hence, the recommendation to exclude an in-depth study of the subject process from the overall scope of work for this project. For a complete explanation of the Significant Emission Index, see Appendix IV of this report.

VI. Vinyl Acetate Producers

	Capacity MM Lbs./Year Acetylene	 Ethylene
Borden Chemical Company	150	
Celanese Chemical Company		
1) Clear Lake, Texas		300*
2) Bay City, Texas		350*
DuPont		300
National Starch & Chemical	56	
Union Carbide	225**	
U. S. Industrial Chemical	____	330
	Total 431	1,280

*Estimated.
**Plant to be phased out by 1974.



ACETYLENE
ACETIC ACID
1
2
3
4
5
6
STEAM
COND.
REACTOR
HEAT MEDIUM
SEPARATOR
ACETIC ACID
VENT
8
LIGHT ENDS COLUMN
VINYL ACETATE COLUMN
7
VINYL ACETATE PRODUCT
HEAVY ENDS COLUMN
INCINERATOR
VENT
10
9
HEAVY ENDS
RECYCLE ACETYLENE
RECYCLE ACETIC ACID

NOTES
NUMBERED STREAMS ARE CROSS REFERENCED
IDENTIFIED FOR MATERIAL BALANCE TABLE I.

ENVIRONMENTAL PROTECTION AGENCY

R-230

A

TABLE VI-1
VINYL ACETATE
FROM
ACETYLENE-ACETIC ACID

MATERIAL BALANCE - T/T VINYL ACETATE

	Fresh Feed	Recycle Acetylene	Recycle Acetic Acid	Gross Feed	Reactor Effluent	Product	Light Ends	Heavy Ends
Acetylene	.3101	1.2699		1.5800	1.2702		.0003	
Acetic Acid	.7440		.1705	.9145	.1737			.0032
Vinyl Acetate					1.0220	1.0000	.0220	
Acetone					.0002		.0002	
Acetaldehyde					.0168		.0168	
Acetic Anhydride					.0016			.0016
Crotonaldehyde					.0007			.0007
Polymer					.0006			.0006
Water					.0087		.0087	
	1.0541	1.2699	.1705	2.4945	2.4945	1.000	.0480	.0061

TABLE VI-II
VINYL ACETATE
FROM
ACETYLENE - ACETIC ACID

GROSS HEAT BALANCE - CONVERTER SECTION ONLY

Heat In (1)

Vaporizer and Preheater	638 (2)
Exothermic Heat of Reaction	577

Total Heat In = 1,215 BTU/lb. of Vinyl Acetate

Heat Out

Maintain Reactants @ Temperature	577
Enthalpy Residual (above base temperature)	638

Total Heat Out = 1,215 BTU/lb. of Vinyl Acetate

NOTE:

(1) Base temperature - 25° C.

(2) Part of preheat generated by exchange with reactor effluent.

TABLE VI-III
NATIONAL EMISSIONS INVENTORY
VINYL ACETATE
VIA
ACETYLENE - ACETIC ACID

Page 1 of 4

Plant EPA Code No.		30-2	
Capacity - Tons of Vinyl Acetate/Yr.		75,000	
Production - Tons of Vinyl Acetate/Yr.		75,000	
Range in Production - % of Max.		0	
Emissions to Atmosphere			
Stream	Absorber Vent		Incineration of Liquid Waste (7)
Flow - Lbs./Hr.	600		1,240
Flow Characteristic, Continuous or Intermittent	Continuous		Continuous
if Intermittent - Hrs./Yr. Flow			
Composition - Tons/Ton Vinyl Acetate			
Acetylene	.02680		
Acetone	.00300		
Acetaldehyde	.00126		
Acetic Acid	.00190		
Vinyl Acetate			
Nitrogen			
CO_2			.04672
H_2O			.01853
NO_x			
Vent Stacks			
Number	3		1
Height - Ft.	80		10
Diameter - Inches	1		96
Exit Gas Temp. - F°	90		3400
Emission Control Devices			
Flare/Incinerator	No		Yes
Analysis			No
Date or Frequency of Sampling	April, 1972		
Sample Tap Location	Not Specified		
Type of Analysis	Gas Chromatograph		
Odor Problem	No		
Summary of Air Pollutants			
Hydrocarbons, Ton/Ton Vinyl Acetate		.02996	
Particulates, Ton/Ton Vinyl Acetate		0	
NO_x Ton/Ton Vinyl Acetate		0	
CO Ton/Ton Vinyl Acetate		0	

TABLE VI-III
NATIONAL EMISSIONS INVENTORY
VINYL ACETATE
VIA
ACETYLENE - ACETIC ACID

Page 2 of 4

Plant EPA Code No.		30-3		
Capacity - Tons of Vinyl Acetate/Yr.		11,250		
Production - Tons of Vinyl Acetate/Yr.		11,250		
Range in Production - % of Max.		0		
Emissions to Atmosphere				
Stream	Converter Purge Gas	Reactor Emergency Vent	Heavy Ends Column Vent	Light Ends Column Vent
Flow - Lbs./Hr.	694	1470	6.3	214 1
Flow Characteristic - Continuous or Intermittent	Intermittent	Intermittent	Continuous	Continuous
If Intermittent, Hrs./Yr. Flow	60	Not Specified		
Composition - Ton/Ton Vinyl Acetate				
Acetylene		+		
Acetone				.00102
Acetaldehyde				00185
Acetic Acid	.00010		.00071	.00285
Vinyl Acetate				
Nitrogen	.00009		.00002	
CO_2		+		
H_2O				
Methyl Acetylene		+	)	)
Propylene		+	)	)
Propane		+	.00227)	.00178)
Methane		+	)	)
Ethane		+	)	)
Ethylene		+	)	)
Vent Stacks	No	Yes	No	No
Number		3		
Height - Ft.		50		
Diameter - Inches		3		
Exit Gas Temp. - F°		110		
Emission Control Devices	No	No	No	No
Flare/Incinerator				
Absorber				
Analysis	None		None	
Date or Frequency of Sampling		Once/Week		3 times a year
Sample Tap Location				Recovery column feed stream
Type of Analysis	Calculated	Mass Spectrometer	Liquid Sampling	Chromatograph
Odor Problem	Yes (1)	Yes (1)	Yes (1) (4)	Yes (1)
Summary of Air Pollutants				
Hydrocarbons, Ton/Ton Vinyl Acetate				
Particulates, Ton/Ton Vinyl Acetate				
NO_x, Ton/Ton Vinyl Acetate				
CO , Ton/Ton Vinyl Acetate				

See Continuation

TABLE VI-III
NATIONAL EMISSIONS INVENTORY
VINYL ACETATE
VIA
ACETYLENE - ACETIC ACID

Page 3 of 4

Plant EPA Code No.		30-3		
Capacity - Tons of Vinyl Acetate/Yr.		11,250		
Production - Tons of Vinyl Acetate/Yr.		11,250		
Range in Production - % of Max.		0		
Emissions to Atmosphere				
Stream	Crude Vinyl Acetate Storage Tank Vents	Refined Vinyl Acetate Storage Tank Vents	Acetic Acid Storage Tank Vents	Incineration of Liquid Waste
Flow - Lbs./Hr.	192.3	35.7 (5)	16.9 (6)	Not Specified (3)
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Intermittent
if Intermittent, Hrs./Yr. Flow				Not Specified
Composition - Ton/Ton Vinyl Acetate				
Acetylene				
Acetone	.00047			
Acetaldehyde	.00284			
Acetic Acid			.00007	
Vinyl Acetate	.00208	.0037		
Nitrogen				
CO_2				.04081
H_2O				01800
Methyl Acetylene				
Prop lene				
Propane				
Methane				
Ethane				
Ethylene				
Vent Stacks	No	No	No	No
Number				
Height - Ft.				
Diameter - Inches				
Exit Gas Temp. - F°				
Emission Control Devices	No	No	No	Yes
Flare/Incinerator				Open air burning
Absorber				
Analysis		None	None	None
Date or Frequency of Sampling	Upon Request			
Sample Tap Location	Liquid Sample			
Type of Analysis	Chromatograph	Estimated	Estimated	Estimated
Odor Problem	Yes (1)	Yes (1)	Yes (1)	No
Summary of Air Pollutants				
Hydrocarbons, Ton/Ton Vinyl Acetate		.01366		
Particulates, Ton/Ton Vinyl Acetate		0		
NO_x, Ton/Ton Vinyl Acetate		0		
CO, Ton/Ton Vinyl Acetate		0		

TABLE VI-III
NATIONAL EMISSIONS INVENTORY
VINYL ACETATE
VIA
ACETYLENE - ACETIC ACID

Page 4 of 4

Plant EPA Code No.		30-4	
Capacity - Tons of Vinyl Acetate/Yr.		28,000	
Production - Tons of Vinyl Acetate/Yr.		28,000	
Range in Production - % of Max		0	
Emissions to Atmosphere			
Stream	Reactor Emergency Vent	Light Ends Column Vent	Incinerated Waste
Flow - Lbs./Hr.	290	269	100
Flow Characteristic, Continuous or Intermittent	Intermittent	Continuous	Intermittent
If Intermittent, Hrs./Yr. Flow	30		156
Composition - Ton/Ton Vinyl Acetate			
Methane	.00004		
Acetylene	.00014	.00025	
Ethylene	.00005		
Acetone		.00020	
Acetaldehyde		.01737	
Acetic Acid			
Vinyl Acetate		.02260	
H_2O			.00340
CO_2			.01100
NO_x			.00006
Particulate			.00002
Vent Stacks			Not Specified
Number	1	1	
Height - Ft.	43	43	
Diameter - Inches	1.5	1.5	
Exit Gas Temp. - F°	185	120	
Emission Control Devices			
Flare/Incinerator			Yes
Analysis			
Date or Frequency of Sampling	Daily	Once	Never
Sample Tap Location	In stream	Vent pipe	
Type of Analysis	Gas Chromatograph	Gas Chromatograph	
Odor Problem	Yes	Yes	No
Summary of Air Pollutants			
Hydrocarbons, Ton/Ton Vinyl Acetate		.04065	
Particulates, Ton/Ton Vinyl Acetate		.00002	
NO_x, Ton/Ton Vinyl Acetate		.00006	
CO , Ton/Ton Vinyl Acetate		0	

TABLE VI-III
NATIONAL EMISSIONS INVENTORY
VINYL ACETATE
FROM
ACETYLENE - ACETIC ACID

EXPLANATION OF NOTES

(1) Odor problem limited to plant property.

(2) Average number of emergency situations a year was not specified.

(3) 804 lbs./hr. of liquid waste burned weekly in open air.

(4) In stream sample taken under ordinary conditions.

(5) 93% air.

(6) 95% air.

(7) Estimated by Houdry assuming total conversion of organics to carbon dioxide and water.

TABLE VI-IV
CATALOG OF EMISSION CONTROL DEVICES
VINYL ACETATE
FROM
ACETYLENE - ACETIC ACID

INCINERATION DEVICES

EPA Code No. for plant using	14-2	14-4
Flow Diagram (Fig. I) Stream I. D.	9	9
Device I. D. No.	VA-1	VA-2
Type of Compound Incinerated	Heavy Liquid Organic Waste	Heavy Liquid Organic Waste
Type of Device - Flare		
Incinerator	X	
Other		Atmospheric Liquid Waste Burner
Material Incinerated - Lb./Hr.	450	804
Auxilliary Fuel Req'd. - Excluding Pilot	No	No
Type		
Rate - BTU/Hr.		
Device or Stack Height - Feet	Not Specified	6
Installed Cost - Mat'l. & Labor - $	210,000	16,000
Installed Cost based on "year" - dollars	1971	1962
Installed Cost - ¢/lb. of Vinyl Acetate	.14	.011
Operating Cost - Annual - $ (1972)	28,000	2,500
Value of Heat or Power Recovery - $/Yr.	0	0
Net Operating Cost - $/Yr.	28,000	2,500
Net Operating Cost - ¢/lb. of Vinyl Acetate	.079	.0017
Efficiency - % - CCR	99.9+	99.9+

TABLE VI-V
NUMBER OF ACETYLENE BASED VINYL ACETATE PLANTS BY 1980

Current Capacity (1)	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Plants
431	225 (2)	206	356	356	150	150	1 (3)

NOTE:

(1) All capacities in MM lbs.

(2) Union Carbide is closing its 225 MM lbs./yr. plant. It is possible that National Starch and Chemical Company's 50 MM plant will be able to stand price pressure,

(3) One new plant of this type is projected on the possibility that raw material costs could make a revised acetylene based plant economically feasible.

TABLE VI-VI
EMISSION SOURCE SUMMARY
TON/TON OF VINYL ACETATE

Emission	Source		Total
	Light Ends Vent	Incineration of Liquid Waste	
Hydrocarbons	.02996	0	.02996
Particulates	0	Negligible	0
NO_x	0	Negligible	0
SO_x	0	0	0
CO	0	0	0

TABLE VI-VII
WEIGHTED EMISSION RATES

Chemical Vinyl Acetate

Process Acetylene - Acetic Acid

Increased Capacity 150

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	.02996	4.5	80	360
Particulates	0	0	60	0
NO_x	0	0	40	0
SO_x	0	0	20	0
CO	0	0	1	0

Significant Emission Index = 360

Vinyl Acetate via Ethylene

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VI.	Vinyl Acetate Producers	VAC-6

List of Illustrations and Tables

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Material Balance	Table VAC-I
Gross Heat Balance	Table VAC-II
Emission Inventory	Table VAC-III
Catalog of Emission Control Devices	Table VAC-IV
Number of New Plants by 1980	Table VAC-V
Emission Source Summary	Table VAC-VI
Weighted Emission Rates	Table VAC-VII

I. Introduction

Vinyl acetate is an important pertochemical used to produce polymer. Most of the vinyl acetate manufactured is polymerized into polyvinyl acetate which is used in latexes, emulsion paints, adhesives and various textile coatings or further processed into polyvinyl alcohol or polyvinyl butyral. About 10 percent is co-polymerized with vinyl chloride, ethylene and other monomers.

Vinyl acetate is currently produced by three processes. The newer two utilize ethylene, oxygen and acetic acid in a vapor or liquid phase reaction. The oldest process, which presently accounts for 30 percent of vinyl acetate production, uses acetylene and acetic acid in a vapor phase reaction. Because of high acetylene raw material costs, little, if any, growth is expected in the acetylene based vinyl acetate industry.

Of the ethylene processes, the vapor phase method is the most popular and future growth is expected in that area. The liquid phase process was tried by Celanese at Bay City, Texas with a 100 MM lbs./year plant. Corrosion problems interrupted production for a while until extensive rebuilding solved these problems.

Currently, there are two patented vapor phase processes available; the U. S. I. Process and the Bayer-Hoechst Process. They both rely on the same reaction scheme, similar catalysts and similar separation techniques. Emissions data found in this report are for a plant using the USI technique. There are two other vinyl acetate plants in the U. S. which rely on ethylene feed, one is operating today and one is in the start-up phase. Both use the Bayer-Hoechst method.

The only emissions reported for the ethylene process were from the flaring of light hydrocarbons and from the incineration of liquid waste. Assuming that complete combustion is achieved the only emissions to the atmosphere are trace amounts of NO_x.

II. Process Description

The following is a description of the USI Vapor Phase Process for vinyl acetate from ethylene, acetic acid and oxygen. The Bayer-Hoechst Process is quite similar and any description of that method would merely be repetitious. (See Fig. VAC-1)

Ethylene, acetic acid and oxygen can react in the vapor phase to produce vinyl acetate and water.

$$C_2H_4 + CH_3COOH + \tfrac{1}{2}\,O_2 \longrightarrow CH_2CHOOCCH_3 + H_2O$$

The reaction takes place in a fixed bed tubular reactor with a supported noble metal catalyst. The reactor operates at 15 to 100 PSIG and below 350° F. The reaction is exothermic and heat is removed on the shell side by cooling water.

Aside from vinyl acetate the reactor effluent consists of water, carbon dioxide, unreacted feed and small quantities of oxygenated hydrocarbons. Carbon dioxide is produced by side combustion reactions, the most important of which is the oxidation of ethylene. The yield is about 91% for vinyl acetate. Of the other 9%, 8% is lost to CO_2 formation and 1% is lost to all other by-products. Conversion is low due to the explosion limit of the ethylene/oxygen mixture.

Prior to introduction in the reactor, acetic acid and ethylene pass to an acid vaporizer where ethylene is saturated with acetic acid to give the required ethylene/acetic acid ratio. The acid tower also serves the purpose of removing any heavy impurities present. Ethylene and acetic acid are superheated upon leaving the vaporizer and mixed with oxygen. This combined stream is fed into the reactor.

Reactor effluent is cooled and sent to an absorber where uncondensed vinyl acetate is absorbed in acetic acid. The absorber off-gas is then water scrubbed to remove any excess acetic acid. The scrubber overhead containing ethylene, carbon dioxide and water is sent to a carbon dioxide absorber where carbon dioxide is removed by potassium carbonate. The overhead contains ethylene, which is recycled to the acid tower. Carbon dioxide is stripped from the potassium carbonate solution and vented to the atmosphere.

Crude vinyl acetate leaving the acetic acid absorber is sent to primary distillation. This system consisting of a distillation column and two auxilliary strippers removes water from the product. Dry vinyl acetate passes to two distillation columns where light ends and heavy ends are removed. The finished vinyl acetate is of a high quality suitable for polymerization.

III. Plant Emissions

A. Continuous Air Emissions

1. Carbon Dioxide Vent

Carbon dioxide, absorbed by potassium carbonate from the non-condensible gas stream is subsequently stripped and vented to the atmosphere. A small amount of water (2.3 vol. %) is carried with the carbon dioxide. No pollutants enter the atmosphere from this vent.

2. Light Ends Flaring

Light hydrocarbons and some inerts, which are purged from the system (from the water scrubber and the light ends distillation column) are mixed with fuel gas and flared. The stream entering the flare consists of ethylene, fuel gas and smaller amounts of oxygen, oxygenated hydrocarbons and inerts such as argon and nitrogen. The respondent claims that the flare is smokeless so it is assumed that combustion is complete to carbon dioxide and water. The only pollutant entering the atmosphere would, therefore, be trace amounts of NO_x and possibly some unburned hydrocarbons.

3. Heavy Ends Incineration

Heavy components removed from the acid vaporization tower and the heavy ends column are burned in an incinerator. The inlet to the incinerator contains acetic acid, mixed glycol diacetates, vinyl acetate, polyvinyl acetate and ethyl acetate. Since no nitrogen or sulfur is present in any of the components burned, the combustion products are carbon dioxide and water. The only air pollutant released is NO_x, which is present in trace amounts.

4. Storage Losses

Vinyl acetate is stored under a blanket and the respondent reports floating roofs will be installed by 1973. Acetic acid is allowed to vent to the atmosphere. On a whole, storage losses should be small.

B. Intermittent Air Emissions

No sources of intermittent air emissions were reported.

C. Continuous Liquid Waste

226 GPM of waste water are produced by the process. The waste is treated on-site.

D. Odor

There does not seem to be an odor problem associated with this process. All vent gases are incinerated to carbon dioxide and water prior to release to the atmosphere.

F. Fugitive Emissions

No emissions due to leaks, spills, etc. were reported.

IV. Emission Control

The emission control devices that have been reported as being employed by vinyl acetate producers using the ethylene process are summarily described in Table IV of this report. An efficiency has been assigned each device wherever data sufficient to calculate it have been made available. Two types of efficiencies have been calculated.*

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} - \frac{\text{lbs. of } O_2 \text{ reacting (with pollutant in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\text{(pollutant x weighting factor)in} - \text{(pollutant x weighting factor)out}}{\text{(pollutant x weighting factor*)in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Emission Control Devices

1) Light Ends Flare

The respondent reports that the flare is smokeless, therefore, complete combustion is assumed and efficiencies are near 100%.

2) Liquid Waste Thermal Oxidizer

This device is included in the Catalog of Emission Control Devices, Table IV even though it releases gases to the atmosphere because it serves the purpose of destroying harmful liquid waste.

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*See Appendix V for a complete explanation of these ratings.

V. Significance of Pollution

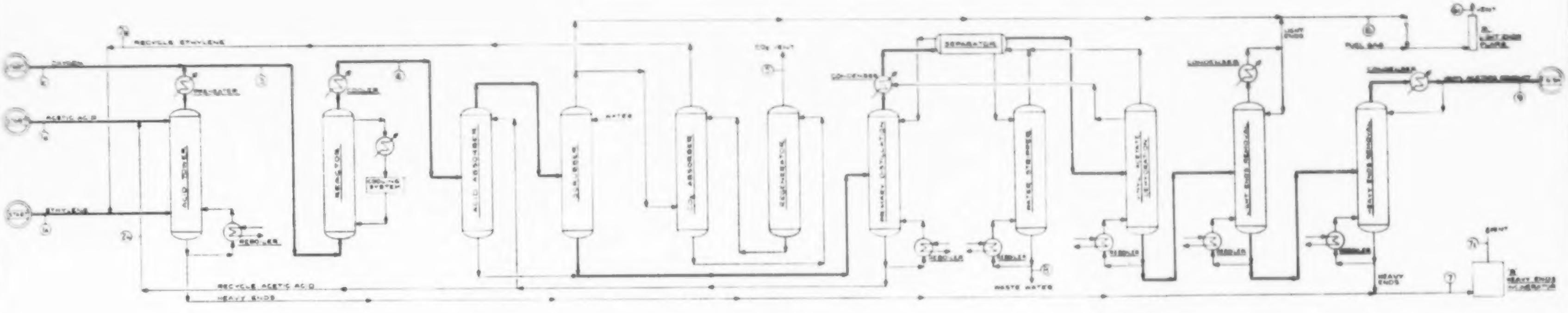
It is recommended that no in-depth study be made of the ethylene process for vinyl acetate. The only pollutant reported as being released to the atmosphere from this process are trace amounts of NO_x. Assuming that any new plant will employ modern technology to control emissions, there should be no need for further study of the subject process.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants by 1980 and to estimate the weighted annual emissions from these new plants. This work is summarized in Tables V, VI and VII.

VI. Vinyl Acetate Producers

Company	Location	Capacity (MM Lbs./Year) Ethylene	Capacity (MM Lbs./Year) Acetylene
Borden Chemical Co.	Geismar, La.		150
Celanese Chemical Co.	Clear Lake, Texas Bay City, Texas	300* 350*	
du Pont	La Porte, Texas	300	
Nat. Starch & Chemical Co.	Long Mott, Texas		56
Union Carbide	Texas City, Texas		225**
U. S. Industrial Chemicals	La Porte, Texas	330	—
	Total =	1,280	431

*Estimated
**Plant to be phased out by 1974


OXYGEN
ACETIC ACID
ETHYLENE
RECYCLE ETHYLENE
PRE-HEATER
ACID TOWER
REBOILER
REACTOR
COOLER
COOLING SYSTEM
ACID ABSORBER
SCRUBBER
WATER
CO2 ABSORBER
REGENERATOR
CO2 VENT
CONDENSER
SEPARATOR
PRIMARY DISTILLATION
WATER STRIPPER
VINYL ACETATE DEHYDRATION
LIGHT ENDS REMOVAL
HEAVY ENDS REMOVAL
LIGHT ENDS
FUEL GAS
VENT
B LIGHT ENDS FLARE
VINYL ACETATE PRODUCT
HEAVY ENDS
A HEAVY ENDS INCINERATOR
WASTE WATER
RECYCLE ACETIC ACID
ENVIRONMENTAL PROTECTION AGENCY
R-239
A

NOTES.
1. NUMBERED STREAMS ARE CROSS REFERENCE IDENTITIES TO MATERIAL BALANCE TABLE I AND NATIONAL EMISSION INVENTORY TABLE II
2. LETTERED EQUIPMENT IS LISTED IN CATALOG OF EMISSION CONTROL DEVICES TABLE III

TABLE VAC-I
MATERIAL BALANCE
VINYL ACETATE
VIA
ETHYLENE PROCESS

Stream I. D. No.	1	2	3	4	5	6	7	8	9
Stream	Fresh Feed	Recycle	Total Feed	Reactor Effluent	CO_2 Purge	Light Ends & Inerts	Heavy Ends	Waste Water	Product
Component									
Ethylene	.3672	3.3048	3.6720	3.3220		.0172			
Acetic Acid	.7152	2.8604 (1)	3.5756	2.8622			.0018		
Oxygen	.2835	(3)	.2835	.0013		.0013			
Argon	.0010	(3)	.0010	.0010		.0010			
Nitrogen	.0004	(3)	.0004	.0004		.0004			
Vinyl Acetate				1.0017		.0002	.0015		1.0000
Carbon Dioxide				.1016	.1016	(4)			
Water		(3)		.2390	.0009	(4)		.2381	
Methyl Acetate				.0001		.0001			
Acrolein				(.0001)		(.0001)			
Acetaldehyde									
Glycol				.0015			.0015		
Polyvinyl Acetate				.0009			.0009		
Ethyl Acetate				.0002			.0002		
Miscellaneous Organics				.0005				.0005 (2)	
	1.3673	6.1652	7.5325	7.5325	.1025	.0203	.0059	.2386	1.0000

(1) Approximate recycle rate based on 10% ethylene conversion and 20% acetic acid conversion.

(2) Estimated.

(3) Recycle actually contains some of these gases, amount has not been estimated.

(4) Scrubber purge also contains some of these gases.

TABLE VAC-II
GROSS HEAT BALANCE (REACTOR SECTION ONLY)
VINYL ACETATE
VIA
ETHYLENE PROCESS

Heat In	BTU/Lb. Vinyl Acetate
Enthalpy of reactants at 177° C (above base temperature*)	1,544
Exothermic heat of reaction**	1,600
	3,144
Heat Out	BUT/Lb. Vinyl Acetate
Heat removed by coolant	1,600
Residual enthalpy (above base temperature)	1,544
	3,144

*Base temperature = 25° C.

**Includes vinyl acetate reaction and the combustion reactions which form CO_2 and H_2O.

TABLE VAC-III
NATIONAL EMISSION INVENTORY
VINYL ACETATE
VIA
ETHYLENE PROCESS

Plant EPA Code No.	30-5		
Capacity - Tons of Vinyl Acetate/Yr.	115,000		
Range in Production - % of Max.	0		
Emissions to Atmosphere			
Stream I. D. No.	5	6_I	7_I
Stream	CO_2 Purge	Light Ends Flame Combustion Gases	Incineration of Liquid Waste
Flow - Lbs./Hr.	3985	14,129	
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow			
Composition			
CO_2	.09627	.06516	.01480
H_2O	.00092	.05534	.00881
N_2		.22311	.04715
NO_x		+	+
Particulate			
Argon		.00100	
Vent Stacks			
Number	1	1	1
Height - Ft. (above grade)	65	100	50
Diameter - Inches	4	14	48
Exit Gas Temp. - F°	110	1000	1600
Emission Control Devices	No	Yes	Yes
Absorber/Scrubber			
Incinerator/Flare		+	+
Analysis	None	None	None
Date or Frequency of Sampling			
Sample Tap Location			
Type of Analysis	Calculated	Calculated	Calculated
Odor Problem	No	No	No
Summary of Air Pollutants			
Hydrocarbons - Ton/Ton of Vinyl Acetate		0	
Particulates - Ton/Ton of Vinyl Acetate		0	
NO_x - Ton/Ton of Vinyl Acetate		+	
SO_x - Ton/Ton of Vinyl Acetate		0	
CO - Ton/Ton of Vinyl Acetate		0	

TABLE VAC-IV
CATALOG OF EMISSION CONTROL DEVICES
VINYL ACETATE
VIA
ETHYLENE PROCESS

INCINERATION DEVICES		
EPA Code No. for plant using	30-5	30-5
Flow Diagram (Fig. I) Stream I.D.	A	B
Device I. D. No.	VAC-I	VAC-II
Type of Compounds Incinerated	Light Hydrocarbons	Liquid Wastes
Type of Device - Flare	Yes	
Incinerator		
Other		Thermal Oxidizer
Material Incinerated (SCFM) Lb./Hr.	1,130	250
Auxilliary Fuel Required - Excluding Pilot		
Type	Natural Gas	Natural Gas
Rate (BTU/Hr.)	1.75×10^6 SCFM	
Device Stack Height - Ft.	100	500
Installed Cost - Mat'l. & Labor - $	67,000	139,000 SCFM
Installed Cost based on "year" - dollars	1970	1970
Installed Cost - ¢/lb. of Vinyl Acetate	.020	.042
Operating Cost Annual - 1972 - $	25,640	44,600
Value of Recovered Product - $/Yr.	0	0
Net Operating Cost - ¢/lb. of Vinyl Acetate	.008	.014
Efficiency - % - CCR	Near 100%	Near 100%
Efficiency - % - SERR	Near 100%	—

TABLE VAC-V
NUMBER OF NEW PLANTS BY 1980
USING ETHYLENE TO PRODUCE VINYL ACETATE

Current (1) Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand (2) 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Plants
(1) 1,280	280	1,000	2,200	2,200	1,200	300	4

(1) MM lbs./year.

(2) Demand for ethylene process assuming very little growth for acetylene process.

TABLE VAC-VI
EMISSION SOURCE SUMMARY
T/T VINYL ACETATE

Emission	Source		Total
	Light Ends Flare	Heavy Ends Thermal Oxidizer	
Hydrocarbons	0	0	0
Particulate	0	0	0
NO_x	Trace	Trace	Trace
SO_x	0	0	0
CO	0	0	0

TABLE VAC-VII
WEIGHTED EMISSION RATES

Chemical Vinyl Acetate

Process Ethylene

Increased Capacity by 1980 1,200 MM Lbs./Year

Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	0	0	80	0
Particulate	0	0	60	0
NO_x	Trace	0	40	0
SO_x	0	0	20	0
CO	0	0	1	0

Significant Emission Index = 0

Vinyl Chloride via EDC Pyrolysis

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V.	Significance of Pollution	VC-8
VI.	VCM Producers	VC-9

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Gross Heat Balance	Table VC-II
Emission Inventory	Table VC-III
Catalog of Emission Control Devices	Table VC-IV
Number of New Plants by 1980	Table VC-V
Emission Source Summary	Table VC-VI
Weighted Emission Rates	Table VC-VII

I. Introduction

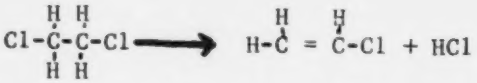
About 90 percent of the vinyl chloride monomer in the United States is produced by cracking dichloroethane. The older process using acetylene and hydrogen chloride feed has been or shortly will be completely replaced by the dichloroethane process because of the high cost of acetylene. The dichloroethane feedstock is produced by either direct chlorination of ethylene, oxychlorination of ethylene or a combination of the two processes. Most of the air emissions associated with production of vinyl chloride monomer originate in the production of dichloroethane and are covered under separate studies of that chemical. Vapor emissions from the cracking operation are small provided that the hydrogen chloride by-product can be recycled to a dichloroethane plant (which is usually the case) or has value for some other operation. In addition to the vapor emissions, a heavy chlorinated hydrocarbon tar is produced which will add to the air pollution problem if this material has to be burned.

A new process has been offered by Lummus Co. (Hydrocarbon Processing, March, 1971, p 11) which produces VCM from ethane, chlorine and air. This process, "Transcat", is reported to have a 1¢/lb. lower VCM manufacturing cost, primarily because of the use of ethane in place of ethylene feedstock. In addition, tar and other chlorinated hydrocarbons are recycled to the cracking reactors so that the process is "free of any known pollution problems", (C & EN, March 1, 1971). A search of the Hydrocarbon Processing world wide boxscore and plant construction does not shown any new vinyl chloride plants presently being built which use the Lummus technology. However, if the process has the reported economic advantage it will probably be incorporated into future VCM construction.

II. Process Description

Dry dichloroethane which is often known as ethylene dichloride, is dehydrochlorinated to vinyl chloride as it passes through the packed tubes of a cracking furnace.

The chemical reaction is:



$$\mathrm{Cl{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}Cl} \longrightarrow \mathrm{H{-}\overset{H}{C} = \overset{H}{C}{-}Cl + HCl}$$

The tubes are normally packed with pumice, charcoal or some other "contact" type catalyst. At 900 to 950° F and 50 PSIG, DCE conversion is about 50 percent and yield to vinyl chloride is 94 to 97 mole percent. The hot effluent gases are then quenched, and partially condensed, by direct contact with cold dichloroethane in a quench tower.

Effluent fractionation and product purification are generally accomplished in three additional towers. However, each producer of VCM has his own minor modifications in the fractionation section. The following description and the Flow Diagram provide generalities about what is achieved by this further processing.

Hydrogen chloride and light chlorinated hydrocarbons are rejected overhead in the "HCL" and "Light Ends" towers. The hydrogen chloride is normally recovered by water scrubbing and recycled to the dichloroethane plant. Trichloroethane, chlorinated C_4's and other heavy ends are rejected from the bottom of either the "quench tower" or the "vinyl tower". Contained dichloroethane is recovered by fractionation and the light and heavy ends are either further processed or disposed of by incineration and other methods. Dichloroethane from the bottom of either the "quench" tower or the "vinyl" tower is recycled to both the quench tower and the feed storage tank. If the DCE is taken from the bottom of the quench tower it is purified before it is recycled. Vinyl chloride monomer is taken overhead in the "vinyl" column, generally caustic washed, and then sent to the product storage facilities.

A "typical" overall material balance is shown in Table I and an estimated cracking furnace heat balance is shown in Table II.

III. Plant Emissions

A. Continuous Air Emissions

1. Cracking Furnace Combustion Stack

All reported operators of plants producing VCM by the pyrolysis of DCE use "sweet" natural gas to fire the cracking furnace. The reported sulfur contents vary between "less than 10 ppm" and "zero". The unit reporting the highest sulfur consumes 60 mm lb/year of gas in the production of 700 mm lb/year of VCM. Therefore, the emission rate is less than 600 lbs/year of sulfur. As SO_2, this is less than 1.7×10^{-6} tons/ton of VCM.

2. By-Product Recovery Systems

All producers of VCM employ scrubbers to recover by-product HCL which is either recycled or used in some other plant process. The non-condensible streams from the HCL recovery sections plus the other light ends from the vinyl chloride purification are either vented, flared, or sent to another process or a pollution control device on another process. This is the main source of air pollution from the process and the reported vent streams, as treated by the various producers, are summarized in Table III.

3. Drier Vent

The pyrolysis process requires the use of dry dichloroethane. The oxychlorination process produces wet dichloroethane. In addition, some reported storage systems employ water seals or water blanketing. Therefore it is presumed that a drying step will be required by some, if not all, process operators. One such operator (EPA Code No. 31-2) reports vent losses from a drying column and these are included in Table III. Since this emission is less than 0.005 tons per ton of VCM, an effort has not been made to contact the other operators to determine if they have a similar vent, or if not, how the DCE is dried. Realistically, the drying step might be considered part of the DCE production process and, therefore, rightfully should be studied in connection with oxychlorination.

4. Storage Losses

Vinyl chloride is stored under pressure, so has no continuous vent losses. Dichloroethane feed is typically stored at atmospheric pressure so that some continuous losses will be experienced. Such devices as nitrogen blanketing, storage under water, or low pressure breather valves are reported with no estimate of actual loss rates given. Presumably, these losses are minimal.

B. Intermittent Air Emissions

1. Cracking Furnace Decoking

Periodically, the process side of the cracking furnace requires decoking. One operator (EPA Code No. 31-8) reported emissions from this operation and they are summarized in Table III. It should be presumed that all operators of dichloroethane cracking furnaces require a similar operation.

2. Start-Up and Emergency Vents

This type of emission is universally encountered in the petrochemical industry and will vary from process-to-process, from operator-to-operator and even from year-to-year. Those which have been reported are included in Table III.

3. Vinyl Chloride Storage

One operator (EPA Code No. 31-8) reports an estimated vinyl chloride loss of 150,000 lbs./year resulting from depressurizing VCM storage for maintenance or relief valve lifting. This is about 0.0002 tons/ton of VCM.

C. Continuous Liquid Wastes

1. Process Tar

All operators report the formation of heavy chlorinated hydrocarbons. These are all reported as going to further processing but might ultimately end up as a waste disposal problem. If incinerated, the problem would be one of air emissions. One operator (EPA Code No. 31-6) reports about one ton per day of this material as "solid" waste. The disposal method is not reported.

2. Drier Column Water

The one operator who reported a drier column included a continuous 0.3 gpm of waste water. Presumably, this is currently discarded but it will eventually go to an overall plant DCE recovery system that is under construction.

3. Vent Scrubbers

One operator (EPA Code No. 31-1) reported 190 gpm of waste water from a vent scrubber. However, the main gas stream to this scrubber is from an oxychlorination unit.

4. Cuastic Washing

One operator (EPA Cdoe No. 31-3) reported a continuous flow of waste caustic from the vinyl chloride washing step. It goes to a pond where it is used to neutralize HCL from other process vents. The quantity of caustic is unreported as is the ultimate pond disposal method. Presumably, all operators must wash the final VCM product with caustic, so all will have spent caustic for disposal.

5. Light Ends

Some operators condense a portion of this material and dispose of it as liquid waste.

D. Intermittent Liquid Wastes

The only reported intermittent water wastes are from emergency and start-up scrubbers, or intermittent spills.

E. Solid Wastes

Solid wastes from the process, are spent catalysts, spent desiccants and broken tower packing. Only one operator (EPA Code No. 31-1) made an estimate of these. However, the questionnaire also covered oxychlorination and direct chlorination processes for the production of DCE so the reported numbers are probably higher than for DCE pyrolysis alone. 425,000 lbs./year of spent materials and 550 cubic yards per year of broken materials were reported. Both are used as land fill within the plant. An estimate of 200 cubic yards per year of miscellaneous trash which is disposed of by a local contractor, was also reported by this operation.

Presumably, disposal of waste salts from vinyl chloride washing with caustic will also be required, especially in the plant that ponds this material.

F. Odors

The questionnaire replies indicate that the cracking of ethylene dichloride is a process with little or no odor problems. All reports on odors indicate that they occur infrequently and (with one exception) only on the plant property. Various chlorinated compounds account for the odors, among these are hydrogen chloride (but only when a scrubber malfunctions), vinyl chloride and ethylene dichloride.

The one report of odors reaching beyond property limits is the flare pond (EPA Code No. 31-3), that is used to incinerate off-gases. This odor has not resulted in any recent complaints, none being reported in the last year.

G. Fugitive Emissions

All respondents report that fugitive emissions are minor. Only one gives an estimate of their magnitudes and that is based on the entire vinyl chloride production facility, including the production of ethylene dichloride by two separate processes. The estimate, having been made by overall material balance is probably not reliable (small difference of large numbers). Thus, there seems little point in reporting it here.

The logical conclusion is that due to the nature of chlorinated hydrocarbons, the operators of this process are careful in their maintenance and sampling and, therefore, achieve minimal fugitive losses.

IV. Emission Control

The various emission control devices that have been reported as being employed by operators of vinyl chloride monomer plants are summarized in Table IV of this report, which is entitled Catalog of Emission Control Devices. The control devices may be divided into two broad categories: (1) Combustion Devices - those devices which depend on thermal or catalytic oxidation of combustibles for emission control, and (2) Non-combustion Devices - devices that do not depend on combustion for emission control. In Table IV, all combustion devices will be assigned two efficiency ratings (when data are available), they are:

(1) CCR - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{Lbs. of } O_2 \text{ that react with pollutants in feed to device}}{\text{Lbs. of } O_2 \text{ that theoretically could react with these pollutants}} \times 100$$

(2) SERR - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\text{weighted pollutants in - weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

A more detailed discussion of these ratings may be found in Appendix V. Whenever data are available, the non-combustion pollution control devices also have been assigned two efficiencies. The first, is merely a calculation of efficiency in the usual sense, that is percent removal of a specific pollutant (or pollutants) for which the device has been designed. However, as also described in Appendix V, many devices do not remove any significant amounts of some pollutants. Thus, a more realistic efficiency rating is the SERR as described above, because it is a measure of the reduction in total pollutants weighted by their noxiousness. In all cases this will either be less than or equal to the efficiency that is usually reported.

One operator (EPA Code No. 31-5) reports scrubber data which are inconsistent. Part III of the questionnaire for streams A & B reports an average removal of 28,600 lbs./hr. of HCL. Yet, Part IV of the questionnaire for device 101 (coded VC-2 in this report), indicates only 200,000 lbs./day total gas flow (8,333 lbs./hr.). The later number is probably correct because it is consistent with the 300 gpm of water to the scrubber and the 8% HCL solution outlet that are reported.

It is unlikely that any change in process operating conditions can be made that will reduce air emissions. Overall selectivities in excess of 94% are reported by all of the process operators, thus it is safe to assume that either a change in catalyst or the use of less severe cracking conditions could only achieve minimal if any improvement in selectivity. Furthermore, most of the non-selective products (light and heavy chlorinated hydrocarbons) are reported to go to other processes where they presumably are converted to marketable or recycleable products. Obviously, any increased severity would result in a lower selectivity and more potential pollution.

There is a possibility that some minor reduction in air emissions could be achieved by the use of a purer raw material. One operator (EPA Code No. 31-3) reports using 497 mm lbs./year of 99.95% DCE as feed, while another (EPA Code No. 31-2) reports using 545 mm lbs./year of 98% DCE as feed. Obviously, the second of these units is required to dispose of more than 10 mm lbs./year of additional organic material. However, since both units have associated side-product recovery systems, this is probably not a pertinent observation, especially since the unit with the more pure feed also reports a greater quantity of air emissions.

Development work directed toward further reductions in emissions from this process falls into the following general categories:

1) Condensation of intermittent releases.

2) Use of vent or waste streams in other processes.

3) More efficient incineration.

4) HCL recovery from incineration.

V. Significance of Pollution

It is recommended that an in-depth study of this process not be undertaken at this time. Although the growth rate of vinyl chloride monomer production by pyrolysis is forecast to be significant, the emission data indicate that the quantity of pollutants from the air emissions is less significant than from many of the other processes that are currently being surveyed.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emissions of pollutants from these new plants. This work is summarized in Tables V, VI, and VII.

Support for the Table V forecast of new plants has appeared in print as recently as May 10, 1972 (Chemical Week, pp 13-14). This article indicates that one new 700 to 800 MM lbs./year plant every 14-18 months from now until 1980 is a reasonable estimate. Thus, the number of new units to be built, especially when the size of each unit is considered, is certainly significant.

However, on a weighted emission basis, a Significant Emission Index (SEI) of 2,159 has been calculated in Table VII. This is substantially less than the SEI's that are anticipated for other processes in the study. Hence, the recommendation to exclude an in-depth study on vinyl chloride monomer production from the scope of work.

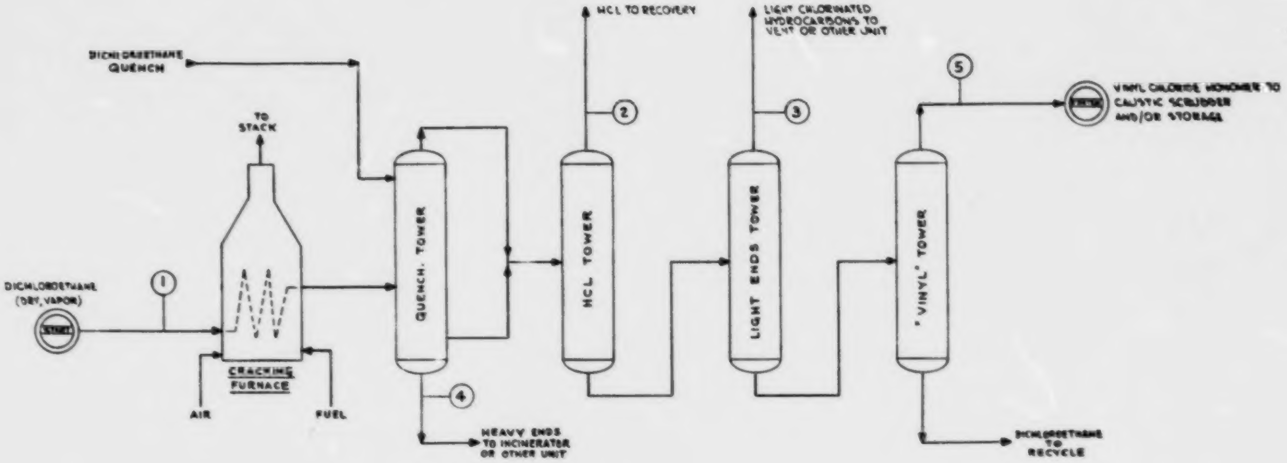
VI. VCM Producers

The following tabulation of producers of vinyl chloride monomer indicates published production capacity by process and location.

Company	Location	Capacity, MM Lbs./Yr.
Allied Chemical	Baton Rouge, La.	300
American Chemical	Long Beach, Cal.	165 - 170
Continental Oil	Lake Charles, La.	600
Dow Chemical	Freeport, Texas	180
	Plaquemine, La.	300 - 340
	Oyster Creek, Texas	800
Ethyl Corporation	Baton Rouge, La.	270
	Pasadena, Texas	150
B. F. Goodrich	Calvert City, Ky.	875 - 1000
PPG Industries	Lake Charles, La.	300
	Guayanilla, P. R.	500 - 575
Shell Chemical	Deer Park, Texas	700
	Sub-Total -	5,140 - 5,385 (1)
Monochem, Inc.	Geismar, La.	300
Tenneco Chemicals	Pasadena, Texas	225 - 250
	Sub-Total -	525 - 550 (2)
	Grand Total -	5,665 - 5,935

(1) All by pyrolysis of idchloroethane.

(2) All by hydrochlorination of acetylene.


DICHLOROETHANE QUENCH
TO STACK
HCL TO RECOVERY
LIGHT CHLORINATED HYDROCARBONS TO VENT OR OTHER UNIT
5
VINYL CHLORIDE MONOMER TO CAUSTIC SCRUBBER AND/OR STORAGE
2
3
DICHLOROETHANE (DRY, VAPOR)
START
1
QUENCH. TOWER
HCL TOWER
LIGHT ENDS TOWER
"VINYL" TOWER
CRACKING FURNACE
AIR
FUEL
4
HEAVY ENDS TO INCINERATOR OR OTHER UNIT
DICHLOROETHANE TO RECYCLE

NOTES:
1. CIRCLED NUMBERS (①) REFER TO MATERIAL BALANCE STREAM NUMBERS.
2. LOCATION OF HEAVY ENDS AND DICHLOROETHANE RECYCLE STREAMS MAY VARY FROM UNIT TO UNIT.

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENN.

FIGURE VC-2
SIMPLIFIED FLOW DIAGRAM
FOR - VINYL CHLORIDE MONOMER PRODUCTION
VIA - DICHLOROETHANE PYROLYSIS

SCALE	NONE	DATE
DRAWN BY	E. ANDERSON	[illegible]
CHECKED BY	[illegible]	[illegible]
CATALYTIC APPROVAL		
CLIENT APPROVAL	[illegible]	[illegible]

PROJECT NO. 42030
LP 411
DWG. NO. R-201
REV. NO. A

TABLE VC-I
VINYL CHLORIDE MONOMER PLANT
NET MATERIAL BALANCE (WEIGHT UNITS)

Component	Fresh Feed	By-Product	Light Hydrocarbons	Heavy Ends Product	Vinyl Chloride Product
HCL		.5835			
Light Hydrocarbons			.0015 (a)		
Dichloroethane	1.6495				
Vinyl Chloride					1.0000 (b)
Heavy Ends				.0645	
	1.6495	.5835	.0015	0.0645 (c)	1.0000

(a) Probably includes ethyl chloride, ethylene, acetylene and chlorine; possibly as large as 4 times value shown.

(b) Includes loading, unloading and storage losses of approximately 0.1%.

(c) Includes vinyl chloride losses; stream probably also consists of trichloroethane, chlorinated C_4's and coke.

TABLE VC-II
VINYL CHLORIDE MONOMER
VIA
DICHLOROETHANE PYROLYSIS
GROSS HEAT BALANCE*

Heat Out

Endothermic heat of reaction		468	BTU/LB. of VCM produced
Quench (to 200° F)		531	" " " "
**Heat losses & inefficiencies		946	" " " "
	Total	1945	

Heat In

Fuel to cracking furnace		1945	BTU/LB. of VCM produced
	Total	1945	" " " "

* Basis

Conversion (DCE) per pass	50%
Selectivity $\frac{\text{(Moles VCM produced)}}{\text{(Moles DCE converted)}}$	96%
Furnace outlet temperature	900° F

** Some portion of the heat in this category is most probably recovered by steam economizer type devices.

TABLE VC-111
EMISSIONS INVENTORY
FOR PRODUCTION OF VINYL CHLORIDE MONOMER BY PYROLYSIS OF DICHLOROETHANE

Page 1 of 6

Company						
Location						
EPA Code Number	31-1		31-2		31-3	
Date on-stream						
Capacity, Tons VCM/Yr.	300,000		165,000		147,500	
Average Production, Tons/Yr.						
Range in Production, % of Max. (a)	0		0		33	
Emissions to Atmosphere						
Stream	Scrubber Effluent	Refrigerant Leakage	Drier Vent	Start-up and Emergency Vent	Quench Tower Vent	Flare Pond
Flow - Lbs./Hour	46,980 (e)	8 (avg.)	200	2,350	686	8,443
Flow Characteristic	Continuous	Variable	Continuous	Intermittent	Intermittent	Continuous
if Intermittent, Hrs./Yr.				0.5	56	
Composition, Tons/Ton VCM						
Dichloroethane	0.00756		0.00137		0.000022	
Vinyl Chloride	0.00109		0.00259		0.000065	
Ethyl Chloride	0.00634		0.00049			
Acetylene						
Hydrogen Chloride	0.00040			< 0.00001	0.000043	0.058
Chlorine	0.00186					
Ethylene	0.00624					
Propylene		0.0001				
Methane	0.00172					
Misc. Chlorinated Hydrocarbons			0.00020			
Carbon Dioxide	0.01440			< 0.00001		0.142
Carbon Monoxide	0.00611					
Nitrogen	0.54999			< 0.00001		
Oxygen	0.02444					
Water	0.00393		0.00024	< 0.00001		0.028
Sample Tap Location	3 feet above grade	None	8 floors above grade	None	None	None
Date or Frequency of Sampling	Weekly	Never	Infrequently	Never	Never	Never
Type of Analysis	GLC & Wet	Calculated	GLC	Calculated	Calculated	Calculated
Odor Problem	Yes (e)	No	No	No	No	Yes
Vent Stacks						
Number	1	1	1	1	1	None (f)
Height, Ft.	148	120	96.5	120	175	
Diameter, Inches	36	8	3	12	4	
Exit Gas Temp. °F	90	80	100 - 120	Very Hot	125	
SCFM Per Stack	11,000 (e)	2.4	17	500	82	
Emission Control Devices (b)						
Water Scrubber	VC - 4			VC - 7		
Incinerator						
Refrigerated Condenser						
Flare				VC - 10		VC - 9
Other or None		None	None		None	
Summary of Air Pollutants	Not Applicable (e)					
Hydrocarbons (c)			0.09465		0.00009	
Particulate (d)			< 0.00001		0.05804	
NO_x						
SO_x						
CO						

TABLE VC-III

EMISSIONS INVENTORY
FOR PRODUCTION OF VINYL CHLORIDE MONOMER BY
PYROLYSIS OF DICHLOROETHANE

Page 2 of 6

Company								
Location								
EPA Code Number	31-4	31-5			31-6			31-7
Date on-stream								
Capacity, Tons VCM/Yr.	(g)	216,000			200,750			(g)
Average Production, Tons/Yr.								
Range in Production, % of Max. (a)		0			0			
Emissions to Atmosphere								
Stream		HCL Tower Non-condensible	Tank Vent	Safety Relief	Scrubber & Stack Seal	Emergency Vent	Loading Vent	
Flow - Lbs./Hour		6	280	3 (i)	Unknown	Unknown	Unknown	
Flow Characteristic		Continuous	Continuous	Continuous		Intermittent	Intermittent	
if Intermittent, Hrs./Yr.						Unknown	Unknown	
Composition, Tons/Ton VCM								
Dichloroethane						3.5%		
Vinyl Chloride		0.000041	0.0055				Trace	
Ethyl Chloride								
Acetylene		0.000082						
Hydrogen Chloride								
Chlorine								
Ethylene								
Propylene								
Methane								
Misc. Chlorinated Hydrocarbons					Trace			
Carbon Dioxide								
Carbon Monoxide								
Nitrogen			0.0001	0.000065	Balance	96.5%	Balance	
Oxygen								
Water		Saturated						
Sample Tap Location		None		None		None	None	
Date or Frequency of Sampling		Never	Never	Never		Never	Never	
Type of Analysis		Calculated	Calculated	Purge Rate	Estimated	Estimated	Estimated	
Odor Problem		No	No	No	No	No	No	
Vent Stacks								
Number		None (h)	1	2	1	1	1	
Height, Ft.			110	110	115	40	(g)	
Diameter, Inches			12	6	4	8	(g)	
Exit Gas Temp. °F		100 - 120	Ambient	Ambient	Ambient	Ambient	Ambient	
SCFM Per Stack		1	29	0.33	Unknown	Unknown	Unknown	
Emission Control Devices (b)								
Water Scrubber		VC - 2			VC - 5	VC - 6		
Incinerator								
Refrigerated Condenser								
Flare								
Other or None			None	None			None	
Summary of Air Pollutants								
Hydrocarbons (c)		0.00012			0.0055			
Particulate (d)								
NO_x								
SO_x								
CO								

TABLE VC-III
NATIONAL EMISSIONS INVENTORY
VINYL CHLORIDE MONOMER PRODUCTION
VIA
PYROLYSIS OF DICHLOROETHANE

Page 3 of 6

Company								
Location								
EPA Code No.	31-7				31-4			
Date on-stream								
Capacity, Tons VCM/Yr.	85,000				432,000			
Average Production, Tons VCM/Yr.					400,000 to 475,000			
Range in Production, % of Max. (a)	0				0			
Emissions to Atmosphere								
Stream	VCM Drier Vent	Distillation Vent Gas Header	EDC Drier Vent	EDC Vaporizer Vent	'Light Ends' Vent	'Light Ends' Vent	'Heavy Ends' Vent	'Heavy Ends' Vent
Flow - lbs./hr.	15 lb./mo.	6080	206	9	200	200	516	5
Flow Characteristic, Continuous or Intermittent if Intermittent, hrs./yr. flow	Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
Composition, Tons/Ton of VCM								
Dichloroethane			.00068	.00008	.00037	.00037	00478	00005
Vinyl Chloride	<.00001				.00037	.00037		
Ethyl Chloride								
Acetylene								
Hydrogen Chloride								
Chlorine								
Ethylene								
Propylene								
Methane								
Misc. Chlorinated Hydrocarbons					.00111	.00111		
Carbon Dioxide		.01056						
Carbon Monoxide			.000121					
Nitrogen	<.00001	.21465						
Oxygen		.05066						
Water		.00958	.00003					
Sample Tap Location	None	None	None	None	None	None	None	None
Date or Frequency of Sampling	Never	Once - 1964			Never	Never	Never	Never
Type of Analysis	Estimate	Various	Estimate	Calc'd.	Calc'd.	Calc'd.	Calc'd.	Calc'd
Odor Problem	No	No	No	No	No	No	No	No
Vent Stacks	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Number		1	1	1	1	1	1	1
Height - Ft.		40	80	80	140	140	44	44
Diameter - Inches		30	1.5	1.5	3	3	3	4
Exit Gas Temp. F°		80	90	120	105	105	120	120
SCFM per stack		1350						
Emission Control Devices (b)	No	Yes - VC-18	VC-11	No	No	No	No	No
Water Scrubber		+						
Incinerator								
Refrigerated Condenser			+					
Other								
Summary of Air Pollutants								
Hydrocarbons	0				See Continuation			
Particulate	0							
NO_x	0							
SO_x	0							
CO	0							

TABLE VC-III
NATIONAL EMISSIONS INVENTORY
VINYL CHLORIDE MONOMER PRODUCTION
VIA
PYROLYSIS OF DICHLOROETHANE

Page 4 of 6

Company			
Location			
EPA Code No.	31-4		
Date on-stream			
Capacity, Tons VCM/Yr.	432,000		
Average Production, Tons VCM/Yr.	400,000 to 475,000		
Range in Production, % of Max. (a)	0		
Emissions to Atmosphere			
Stream	Topping Column Off-Gas	Heavy Ends Recovery Vent	Flare Flue Gas
Flow - lbs./hr.	30	5	Not Specified
Flow Characteristic, Continuous or Intermittent	Continuous	Continuous	Continuous
If Intermittent hrs./yr. flow			
Composition - Tons/Ton of VCM			
Dichloroethane	.00006	.00005	
Vinyl Chloride			
Ethyl Chloride			
Acetylene			
Hydrogen Chloride			~ 00007
Chlorine			
Ethylene			
Propylene			
Methane			
Misc. Chlorinated Hydrocarbons	.00016		
Carbon Dioxide			+
Carbon Monoxide			
Nitrogen			+
Oxygen			+
Water			+
Sample Tap Location			
Date or Frequency of Sampling	Never	Never	Never
Type of Analysis	Calc'd.	Calc'd.	Calc'd
Odor Problem	No	No	No
Vent Stacks	Yes	Yes	Yes
Number	1	1	1
Height - Ft.	46	58	150
Diameter - Inches	2	3	24
Exit Gas Temp. - F^{o}	120^{o}	90^{o}	
SCFM per stack			
Emission Control Devices (b)		No	VC-16
Water Scrubber			
Incinerator			
Refrigerated Condenser	VC-12		
Other			Flare
Summary of Air Pollutants			
Hydrocarbons		.00956	
Particulate		.00007	
NO_x			
SO_x			
CO			

TABLE VC-III
EMISSIONS INVENTORY
FOR PRODUCTION OF VINYL CHLORIDE MONOMER BY PYROLYSIS OF DICHLOROETHANE

Page 5 of 6

Company					
Location					
EPA Code Number		31-8			
Date on-stream					
Capacity, Tons VCM/Yr.		350 000			
Average Production, Tons/Yr.					
Range in Production, % of Max. (a)		0			
Emissions to Atmosphere					
Stream	Various Tower Overheads	Storage Vent		Maintenance Vent	Furnace Decoking
Flow - lbs./Hour	198 (j)	18 (avg.)		1,000 (lbs./yr.)	30 000
Flow Characteristic	Continuous	Intermittent		Intermittent	Intermittent
if Intermittent, Hrs./Yr		Unknown		Unknown	50 - 100
Composition, Tons/Ton VCM					
Dichloroethane				6%	Trace
Vinyl Chloride	0.0023	0.00021			
Ethyl Chloride					
Acetylene					
Hydrogen Chloride				Trace	
Chlorine					
Ethylene					
Propylene					
Methane					
Misc. Chlorinated Hydrocarbons				Trace	
Carbon Dioxide					Unknown
Carbon Monoxide					Unknown
Nitrogen				Balance	
Oxygen					Mostly
Water					
Sample Tap Location	None	None		None	None
Date or Frequency of Sampling	Never	Never		Never	Never
Type of Analysis	Calculated	Calculated		Estimated	Air & Stream Meters
Odor Problem	No	No			
Vent Stacks					
Number	1	1		1	1
Height, Ft.	110	75		40	40
Diameter, Inches	30	7		8	12
Exit Gas Temp. °F	60 - 100	Ambient		Ambient	212
SCFM Per Stack	20 (j)	2 (avg.)		7,000 - 14 000 (CFY)	6,000
Emission Control Devices (b)					
Water Scrubber	VC - 3				VC - 1
Incinerator					
Refrigerated Condenser					
Flare					
Other or None		None		None	
Summary of Air Pollutants					
Hydrocarbons (c)			0.00251		
Particulate (d)			Trace		
NO_x					
SO_x					
CO			Trace		

TABLE VC-III
EXPLANATION OF NOTES
EMISSIONS INVENTORY
FOR PRODUCTION OF VINYL CHLORIDE MONOMER BY PYROLYSIS OF DICHLOROETHANE

Page 6 of 6

(a) Difference between maximum & minimum quarterly production divided by maximum quarterly production.

(b) See Table IV, Catalog of Emission Control Devices for details.

(c) Includes H_2S. Excludes CH_4 & H_2.

(d) Includes aerosols such as HCl and Cl_2.

(e) Unspecified portion of this stream results from dichloroethane production.

(f) Stream is vented below surface of pond, combustibles burn at pond surface.

(g) No data received.

(h) Vents from top of 14 foot scrubber tower.

(i) Purged Header - pollutants will increase during emergencies or relief valve lifitng.

(j) Minor portion of a combined vent from other process.

TABLE VC-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF VINYL CHLORIDE MONOMER VIA THE PYROLYSIS OF DICHLOROETHANE

Page 1 of 6

	Cracking Furnace	HCl Tower OVHD			Recycle Dichloroethane Purification	Emergency Vents	
WATER SCRUBBERS - Flow diagram stream I. D.							
Device I. D. Number	(VC - 1)	(VC - 2)	(VC - 3)	(VC - 4)	(VC - 5)	(VC - 6)	(VC - 7)
EPA Code No. for plant using	31-8	31-5	31-8	31-1	31-6	31-6	31-2
Purpose - Control Emission of	Coke particles	HCL	HCL	HCL	DCE & Lt. H.C.	Lt H.C.	Lt. H.C.
Type - Spray				X			
Packed Column					X	X	
Trays - Type		X - seive					
Number		10					
Plenum Chamber	X						
Other			Not Specified	w/Venturi Mixer			Not Specified
Water Rate - GPM	20	300		500 - 650	50	130	
Design Temp. (operating temp.) - F°	212	(Ambient)		90	190	250	
Gas Rate - SCFM (lb./hr.)	6,000	(8,333)	20	11,000 (A)	1,200	5,800	
T-T Height - Ft.	10	14	Not Specified	50	12	16	
Diameter - Ft	6	3		10	3	4	
Washed Gases to Stack	Yes	No		Yes	Yes	Yes	(To flare)
Stack Height - Ft.	40			148	115	40	120
Stack Diameter - Ft.	1			3	4	.7	1
Installed Cost - Material & Labor - $	24,000	5,500		214,000	5,900	10,700	107,600
Installed Cost - ¢/lb. of VCM/Yr.	.0034	.0013			.0015	.0027	.0326
Operating Cost - Annual - $	1,200	1,000		50,000	1,550	58,940	25,000
Operating Cost - ¢/lb. of VCM	.0002	.0003			.0004	.0147	.0076
Efficiency %	Not Specified	99.98		88.5	Not Specified	Not Specified	100
Efficiency - SERR %		99.95		15			96.0

TABLE VC-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF VINYL CHLORIDE MONOMER VIA THE PYROLYSIS OF DICHLOROETHANE

Page 2 of 6

REFRIGERATED CONDENSER & K. O. DRUM - Flow Daigram Stream I. D.	HCL Tower OVHD
Device I. D. Number	(VC - 8)
EPA Code No. for plant using	31-1
Purpose	Recover DCE (B)
Primary Refrigeration Liquid	Propylene
Capacity of Refrigeration Unit-Tons	230
Gas Rate - SCFM	11,400
Temperature to cooler - °F	95
Temperature - K. O. Drum - °F	-10
Liquid Recovered - GPM	10
Non-condensibles - SCFM	11,000
Installed Cost - Material & Labor - $	525,000
Installed Cost - ¢/lb. of VCM	
Operating Cost - Annual - $	- 1,052,000
Operating Cost - ¢/lb. of VCM	
Efficiency %	80
SERR %	72.5

TABLE VC-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF VINYL CHLORIDE MONOMER VIA THE PYROLYSIS OF DICHLOROETHANE

Page 3 of 6

INCINERATION DEVICES - Flow Diagram Stream I. D.		
Device I. D. Number	(VC - 9)	(VC - 10)
EPA Code No. for plant using	31-3	31-2
Types of Compounds Incinerated	Lt. H. C.	Lt. H. C.
Type Device - Flare		X
Incinerator		
Other	X	
Materials Incinerated SCFM (lb./hr.)	(22)	(360)
Auxilliary Fuel Req'd (excluding pilot)	No	None
Auxilliary Fuel Type		
Auxilliary Fuel Rate - BTU/Hr.		
Device Elevation - Ft. above grade	0	120
Installed Cost - Material & Labor - $	65,000	Not Specified
Installed Cost - ¢/lb. of VCM/Yr.	.0220	
Operating Cost - Annual - $	14,500	
Operating Cost - ¢/lb. of VCM	.0049	
Efficiency - CCR - %	100	100
Efficiency - SERR - %	53.8 (H)	56.0

TABLE VC-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN PRODUCTION OF VINYL CHLORIDE MONOMER VIA THE PYROLYSIS OF DICHLOROETHANE

Page 4 of 6

REFRIGERATED CONDENSER & K. O. DRUM

Flow Diagram Stream I.D.		3	4	4	5
Device I.D. No.	VC-11	VC-12	VC-13	VC-14	VC-15
EPA Code No. for plant using	31-4	31-4	31-4	31-4	31-4 (F)
Purpose - Control emission of	EDC	Chlorinated HC	Chlorinated HC	Chlorinated HC	VCM
Primary Refrigeration Liquid	Water	Brine	Water	Water	Water
Capacity of Refrigeration, Unit-Tons					
Gas Rate SCFM (lb./hr.)	(369)	(200)			
Temperature to cooler - F	90°	50°	90°	90°	102°
Temperature out of cooler - F°					
Liquid Recovered - GPM (lb./hr.)	(236) of EDC	(170)			
Non-Condensibles - SCFM (lb./hr.)	(116)	(30)			
Installed Cost - Mat'l. & Labor - $	4000	450C	4000	4000	66000
Installed Cost - Mat'l. & Labor - ¢/lb. of VCM-Yr.	.00046	.00052	.00046	.00046	.00764
Operating Cost - Annual - $	-44,500	900 (E)	1000 (E)	1000 (E)	- 45.500
Operating Cost - ¢/lb. of VCM		.00010	.00012	.00012	
Efficiency and SERR %	85.3	85.0			

INCINERATION DEVICES

Flow Diagram Stream I.D.	3
Device I.D. No.	VC-16
EPA Code No. for plant using	31-4
Types of Compounds Incinerated	Misc. HC
Type Device - Flare	+
Incinerator	
Other	
Materials Incinerated SCFM (lb./hr.)	
Auxilliary Fuel Req'd. (excluding pilots)	
Auxilliary Fuel Type	
Auxilliary Fuel Rate - BTU/hr.	
Device Elevation - Ft. above grade	
Installed Cost - Mat'l. & Labor - $	300,000
Installed Cost - Mat'l. & Labor - ¢/lb. of VCM	.03472
Operating Cost - Annual - $	8.000
Operating Cost - ¢/lb. of VCM	.00093
Efficiency - CCR - %	100
Efficiency - SERR - %	∠100

TABLE VC-IV
CATALOG OF EMISSION CONTROL DEVICES
CURRENTLY USED IN PRODUCTION OF
VINYL CHLORIDE MONOMER
VIA THE
PYROLYSIS OF DICHLOROETHANE

Page 5 of 6

WATER SCRUBBERS

Flow Diagram Stream I.D.	2-3-4-5	2
Device I.D. No.	VC-18	VC-17
EPA Code No. for plant using	31-7	31-4
Purpose - Control emission of	Chlorinated Hydrocarbons	HCL
Type - Spray		
Packed Column	+	
Trays - Type		
Number		
Plenum Chamber		
Other	+ (G)	+ (Pond)
Water Rate - GPM	25-50	
Design Temp. (Operating Temp.) F°	(80)	Ambient
Gas Rate SCFM (lb./hr.)	1350	
T-T Height - Ft.	40	
Diameter - Ft.	4.5	
Washed Gases to Stack	Yes	No
Stack Height - Ft.	40	
Stack Diameter - Ft.	2.5	
Installed Cost - Mat'l. & Labor - $	150,000	40,000
Installed Cost - Mat'l. & Labor - ¢/Lb. VCM-Yr.	.05555	.00463
Operating Cost - Annual - $	15,600	16,000
Operating Cost - ¢/lb. of VCM	.00578	.00185
Efficiency - % (D)		

TABLE VC-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF VINYL CHLORIDE MONOMER VIA THE PYROLYSIS OF DICHLOROETHANE

(A) Treats effluents from direct chlorination, oxychlorination and "various relief systems in plant" in addition to indicated stream.

(B) Recovers DCE from oxychlorination process.

(C) All plant waste streams pumped to waste pond. Flammable materials burnt at pond's surface.

(D) Defined as percent removal of total air pollutants in stream being treated.

(E) In addition to listed operating cost, respondent added $139,325/year for off-site disposal (incineration).

(F) This device consists of a compressor and condensor, for recovery of VCM vapors from tank cars.

(G) This complex device consists of:

(1) Two Parallel Vent Gas Scrubbers

@ 35' T-T, 24" dia., packed with raschig rings and intalox saddles, 5 - 10 GPM caustic circ.

(2) Waste Gas Boiler

10,000 lbs./hr., 250 psig steam
600° F operating temperature

(3) Final flue gas scrubber - See Table IV

Costs listed are for all equipment.

(H) 53.8% = SERR efficiency for combustion process only, for pond & flare SERR = 66.5% (assumes pond absorbs all HCL in feed to flare).

TABLE VC-V
NUMBER OF NEW PLANTS BY 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
VCM	DCE Pyrolysis	5,400	500	4,900	12,000	13,000	8,100	800	10
	Acetylene	550	550	0	0	0	0	0	0

Note: All capacities in mm lbs./year.

TABLE VC-VI
SUMMARY OF EMISSION SOURCES*

	Source							
Pollutant	EDC Drier and Vaporizer plus VCM Drier	Cracking Furnace	Quench Tower	HCL Tower	"Light Ends" Reject	"Heavy Ends" Reject	Storage Losses and Fugitive Emissions	Total
Hydrocarbons	.00100		.00005	.00010	.00100	.00100	.00010	.00325
Particulates			.00001	.00010				.00011
NO_x		TR						TR
SO_x		TR						TR
CO								

*Pollutant concentrations in lbs./lb. of VCM.

TABLE VC-VII
WEIGHTED EMISSION RATES

Chemical VCM

Process DCE Pyrolysis

Increased Capacity by 1980 8,100 MM Lbs./Year

Pollutant	Emissions Lbs./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	0.00325	26.33	80	2,106
Particulates	0.00011	0.89	60	53
NO_x	TR		40	
SO_x	TR		20	
CO			1	

Significant Emission Index = 2,159

APPENDIX I

FINAL ADDRESS LIST

Air Products & Chemicals, Inc.
P. O. Box 97
Calvert City, Kentucky

Attention: Mr. Howard Watson

Allied Chemical Corp.
Morristown, New Jersey

Attention: Mr. A. J. VonFrank
Director Air & Water
Pollution Control

American Chemical Corp.
2112 E. 223rd
Long Beach, California 90810

Attention: Mr. H. J. Kandel

American Cyanamid Company
Bound Brook, New Jersey

Attention: Mr. R. Phelps

American Enka Corporation
Enka, North Carolina 28728

Attention: Mr. Bennet

American Synthetic Rubber Corp.
Box 360
Louisville, Kentucky 40201

Attention: Mr. H. W. Cable

Amoco Chemicals Corporation
130 E. Randolph Drive
Chicago, Illinois

Attention: Mr. H. M. Brennan, Director
of Environomental Control Div.

Ashland Oil Inc.
1409 Winchester Ave.
Ashland, Kentucky 41101

Attention: Mr. O. J. Zandona

Borden Chemical Co.
50 W. Broad Street
Columbus, Ohio 43215

Attention: Mr. Henry Schmidt

Celanese Chemical Company
Box 9077
Corpus Christi, Texas 78408

Attention: Mr. R. [illegible]. Maurer

Chemplex Company
3100 Gulf Road
Rolling Meadows, Illinois 60008

Attention: Mr. P. Jarrat

Chevron Chemical Company
200 Bush Street
San Francisco, California 94104

Attention: Mr. W. G. Toland

Cities Service Inc.
70 Pine Street
New York City, NY 10005

Attention: Mr. C. P. Goforth

Clark Chemical Corporation
Blue Island Refinery
131 Kedzie Avenue
Blue Island, Illinois

Attention: Mr. R. Bruggink, Director
of Environmental Control

Columbia Nitrogen Corporation
Box 1483
Augusta, Georgia 30903

Attention: Mr. T. F. Champion

Continental Chemical Co.
Park 80 Plaza East
Saddlebrook, NJ 07662

Attention: Mr. J. D. Burns

Cosden Oil & Chemical Co.
Box 1311
Big Spring, Texas 79720

Attention: Mr. W. Gibson

Dart Industries, Inc.
P. O. Box 3157
Terminal Annex
Los Angeles, California 90051

Attention: Mr. R. M. Knight
Pres. Chemical Group

Diamond Plastics
P. O. Box 666
Paramount, California 70723

Attention: Mr. Ben Wadsworth

Diamond Shamrock Chem. Co.
International Division
Union Commerce Building
Cleveland, Ohio 44115

Attention: Mr. W. P. Taylor, Manager
Environ. Control Engineering

Dow Badische Company
Williamsburg, Virginia 23185

Attention: Mr. L. D. Hoblit

Dow Chemical Co. - USA
2020 Building
Abbott Road Center
Midland, Michigan 48640

Attention: Mr. C. E. Otis
Environmental Affairs Div.

E. I. DuPont de Nemours & Co.
Louviers Building
Wilmington, Delaware 19898

Attention: Mr. W. R. Chalker
Marketing Services Dept.

Eastman Chemicals Products, Inc.
Kingsport, Tennessee

Attention: Mr. J. A. Mitchell
Executive Vice President
Manufacturing

El Paso Products Company
Box 3986
Odessa, Texas 79760

Attention: Mr. N. Wright,
Utility and Pollution
Control Department

Enjay Chemical Company
1333 W. Loop South
Houston, Texas

Attention: Mr. T. H. Rhodes

Escambia Chemical Corporation
P. O. Box 467
Pensacola, Florida

Attention: Mr. A. K. McMillan

Ethyl Corporation
P. O. Box 341
Baton Rouge, Louisiana 70821

Attention: Mr. J. H. Huguet

Fibre Industries Inc.
P. O. Box 1749
Greenville, South Carolina 29602

Attention: Mr. Betts

Firestone Plastics Company
Box 699
Pottstown, Pennsylvania 19464

Attention: Mr. C. J. Kleinart

Firestone Synthetic Rubber Co.
381 W. Wilbeth Road
Akron, Ohio 44301

Attention: Mr. R. Pikna

Firestone Plastics Company
Hopewell, Virginia

Attention: Mr. J. Spohn

FMC - Allied Corporation
P. O. Box 8127
South Charleston, W. VA 25303

Attention: Mr. E. E. Sutton

FMC Corporation
1617 J.F.K. Boulevard
Philadelphia, PA

Attention: Mr. R. C. Tower

Foster Grant Co., Inc.
289 Main Street
Ledminster, Mass. 01453

Attention. Mr. W. Mason

G.A.F. Corporation
140 W. 51st Street
New York, NY 10020

Attention: Mr. T. A. Dent, V.P.
of Engineering

General Tire & Rubber Company
1 General Street
Akron, Ohio 44309

Attention: Mr. R. W. Laundrie

Georgia-Pacific Company
900 S.W. 5th Avenue
Portland, Oregan 97204

Attention: Mr. V. Tretter
Sr. Environmental Eng.

Getty Oil Company
Delaware City, Delaware 19706

Attention: Mr. Gordon G. Gaddis

B. F. Goodrich Chemical Co.
6100 Oak Tree Blvd.
Cleveland, Ohio 44131

Attention: Mr. W. Bixby

Goodyear Tire & Rubber Co.
1144 E. Market Street
Akron, Ohio 44316

Attention: Mr. B. C. Johnson, Manager
Environmental Engineering

Great American Chemical Company
650 Water Street
Fitchburg, Mass.

Attention: Dr. Fuhrman

Gulf Oil Corporation
Box 1166
Pittsburgh, Pennsylvania

Attention: Mr. D. L. Matthews
Vice President -
Chemicals Department

Hercules Incorporated
910 Market Street
Wilmington, Delaware

Attention: Dr. R. E. Chaddock

Hooker Chemical Corporation
1515 Summer Street
Stamford, Conn. 06905

Attention: Mr. J. Wilkenfeld

Houston Chemical Company
Box 3785
Beaumont, Texas 77704

Attention: Mr. J. J. McGovern

Hystron Fibers Division
American Hoechst Corporation
P. O. Box 5887
Spartensburg, SC 29301

Attention: Dr. Foerster

Jefferson Chemical Company
Box 53300
Houston, Texas 77052

Attention: Mr. M. A. Herring

Koch Chemical Company
N. Esperson Building
Houston, Texas 77002

Attention: Mr. R. E. Lee

Koppers Company
1528 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. D. L. Einon

Marbon Division
Borg-Warner Corporation
Carville, Louisiana 70721

Attention: Mr. J. M. Black

Mobay Chemical Corporation
Parkway West & Rte 22-30
Pittsburgh, Pennsylvania 15205

Attention: Mr. Gene Powers

Mobil Chemical Company
150 E. 42nd Street
New York, NY 10017

Attention: Mr. W. J. Rosenbloom

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Attention: Mr. J. Depp, Director of
Corp. Engineering

National Distillers & Chem. Corp.
U.S. Industrial Chem. Co. Div.
99 Park Avenue
New York, NY 10016

Attention: Mr. J. G. Couch

National Starch & Chem. Co.
1700 W. Front Street
Plainfield, New Jersey 07063

Attention: Mr. Schlass

Northern Petrochemical Company
2350 E. Devon Avenue
Des Plaines, Illinois 60018

Attention: Mr. N. Wacks

Novamont Corporation
Neal Works
P. O. Box 189
Kenova, W. Virginia 25530

Attention: Mr. Fletcher

Olin Corporation
120 Long Ridge Road
Stamford, Conn.

Attention: Mr. C. L. Knowles

Pantasote Corporation
26 Jefferson Street
Passaic, New Jeresy

Attention: Mr. R. Vath

Pennwalt Corporation
Pennwalt Building
3 Parkway
Philadelphia, PA 19102

Attention: Mr. J. McWhirter

Petro-Tex Chemical Corporation
Box 2584
Houston, Texas 77001

Attention: Mr. R. Pruessner

Phillips Petroleum Co.
10 - Phillips Bldg.
Bartlesville, Oklahoma 74004

Attention: Mr. B. F. Ballard

Polymer Corporation, Ltd.
S. Vidal Street
Sarnia, Ontario
Canada

Attention: Mr. J. H. Langstaff
General Manager
Latex Division

Polyvinyl Chemicals Inc.
730 Main Street
Wilmington, Mass. 01887

Attention: Mr. S. Feldman, Director of
Manufacturing - Engineering

PPG Industries Inc.
One-Gateway Center
Pittsburgh, Pennsylvania 15222

Attention: Mr. Z. G. Bell

Reichold Chemicals Inc.
601-707 Woodward Hts. Bldg.
Detroit, Michigan 48220

Attention: Mr. S. Hewett

Rohm & Haas
Independence Mall West
Philadelphia, PA 19105

Attention: Mr. D. W. Kenny

Shell Chemical Co.
2525 Muirworth Drive
Houston, Texas 77025

Attention: Dr. R.L. Maycock
Environ. Eng. Div.

Sinclair-Koppers Chem. Co.
901 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. R. C. Smith

Skelly Oil Company
Box 1121
El Dorado, Kansas 67042

Attention: Mr. R. B. Miller

Standard Brands Chem. Industries
Drawer K
Dover, Delaware 19901

Attention: Mr. E. Gienger, Pres.

Stauffer Chemical Co.
Westport, Connecticut

Attention: Mr. E. L. Conant

Stepan Chemical Company
Edens & Winnetka Road
Northfield, Illinois 60093

Attention: Mr. F. Q. Stepan
V.P. - Industrial Chemicals

Tenneco Chemicals Inc.
Park 80 Plaza - West 1
Saddlebrook, NJ 07662

Attention: Mr. W. P. Anderson

Texas - U.S. Chemical Company
Box 667
Port Neches, Texas 77651

Attention: Mr. H. R. Norsworth

Thompson Plastics
Assonet, Mass. 02702

Attention: Mr. S. Cupach

Union Carbide Corporation
Box 8361
South Charleston, W. Virginia 25303

Attention: Mr. G. J. Hanks, Manager
Environ. Protection
Chem. & Plastics Division

Uniroyal Incorporated
Oxford Management &
Research Center
Middlebury, Conn. 06749

Attention: Mr. F. N. Taff

The Upjohn Company
P. O. Box 685
La Porte, Texas

Attention: Mr. E. D. Ike

USS Chemicals Division
U.S. Steel Corporation
Pittsburgh, Pennsylvania 15230

Attention: Mr. Gradon Willard

W. R. Grace & Company
3 Hanover SquarNew York, NY 10004

Attention: Mr. Robt. Goodall

Wright Chemical Corporation
Acme Station
Briegelwood, North Carolina 28456

Attention: Mr. R. B. Catlett

Wyandotte Chemical Corp.
Wyandotte, Michigan 48192

Attention: Mr. John R. Hunter

Vulcan Materials Company
Chemicals Division
P.O. Box 545
Wichita, Kansas 67201

Attention: H.M. Campbell
Vice-President, Production

ENVIRONMENTAL PROTECTION AGENCY

Office of Air Programs
Research Triangle Park, North Carolina 27711

Dear Sir:

The Environmental Protection Agency, Office of Air Programs is engaged in a study of atmospheric emissions from the Petrochemical Industry. The primary purpose of this study is to gather information that will be used to develop New Stationary Source Performance Standards which are defined in Section 111 of the Clean Air Act as amended December 31, 1970 (Public Law 91604). These new source standards will not be set as part of this study but will be based (to a large extent) on the data collected during this study.

A substantial part of the work required for this study will be performed under contract by the Houdry Division of Air Products and Chemicals. Several other companies not yet chosen will assist in the source sampling phase of the work.

Very little has been published on atmospheric emissions from the petrochemical industry. The first part of this study will therefore rank the most important petrochemical processes in their order of importance in regard to atmospheric emissions. The Petrochemical Emissions Survey Questionnaire will be the primary source of data during the first phase. This ranking will be based on the amount and type of emissions from the process, the number of similar processes and the expected growth of the process. A second in-depth phase of the study to document emissions more completely will be based on information obtained through actual stack sampling.

Attached you will find a copy of the petrochemical questionnaire which you are requested to complete and return to the Enviromental Protection Agency within forty-two (42) calender days.

You are required by Section 114 of the Clean Air Act to complete each applicable part of this questionnaire except for question II.4. and II.5. These two questions are concerned with the water and solid waste generated by the process itself not with that generated by the emission control equipment. This information would be of a value to the EPA and your answers will be appreciated.

This questionnaire is to be completed using the information presently available to your company. We are not asking that you perform special non-routine measurements of emissions streams. We are asking for results of measurements that you have made or for estimates when measurements have not been made. Where requested information is not available, please mark sections "not available". Where the requested information is not applicable to the subject process, mark the questionnaire sections "not applicable". A sample questionnaire, filled out for a fictitious process is enclosed for your guidance.

It is the opinion of this office that for most processes it should be possible to answer all survey questions without revealing any confidential information or trade secrets. However, if you believe that any of the information that we request would reveal a trade secret if divulged you should clearly identify such information on the completed questionnaire. Submit, with the completed questionnaire, a written justification explaining the reason for confidential status for each item including any supportive data or legal authority. Forward a duplicate of your claim and supporting material, without the questionnaire data, to our counsel, Mr. Robert Baum, Assistant General Counsel, Air Quality and Radiation Division, Environmental Protection Agency, Room 17B41, 5600 Fishers Lane, Rockville, Maryland 20852. Emission data cannot be considered confidential.

Final authority for determining the status of the information resides with the Enviromental Protection Agency. A reply describing the decision reached will be made as soon as possible after receipt of the claim and supporting information. During the period before the final determination this office will honor any request to treat the questionnaire information as confidential.

Information declared to be a trade secret is subject to protection from being published, divulged, disclosed or made known in any manner or to any extent by Section 1905 of Title 18 of the United States Code. The disclosure of such information, except as authorized by law, shall result in a fine of not more than $1,000 or imprisonment of not more than one year, or both; and shall result in removal of the individual from his office or employment.

Although it should be noted that Section 114, Subsection C of the Clean Air Act allows such information to be disclosed "to other officers, employees, or authorized representatives of the United States concerned with carrying out the Act or when relevant in any proceeding under this Act," no confidential information will be revealed to any private concern employed by the Environmental Protection Agency to assist in this study.

The handling and storage of information for which the determination is pending or information which has been determined to be of a confidential nature is carefully controlled. Preliminary control procedures require that the material be labeled confidential and stored in a locked file.

The complete form should be mailed to:

Mr. Leslie B. Evans
Environmental Protection Agency
Office of Air Programs
Applied Technology Division
Research Triangle Park, NC 27711

It is possible that additional copies of this questionnaire which will request information covering other petrochemical processes or other plants using the same process and operated by your organization will be sent to you in the course of this study. Clarification of items contained in the questionnaire may be obtained from Mr. Evans by telephone at 919/688-8146. Thank your for your help in this matter.

Sincerely,

Leslie B. Evans

Leslie B. Evans
Industrial Studies Branch

Petrochemical Questionnaire

Instructions

I. Capacity. Describe capacity of process by providing the following:

1. Process capacity. Give capacity in units per year and units per hour. An "actual" capacity is preferred but "published" or "name plate" capacity will be satisfactory if such capacity is reasonably correct. Do not give production.

2. Seasonal variation. Describe any significant seasonal variations in production.

   As example an ammonia plant might produce more during spring and winter quarters:

quarter	Jan-Mar	April-June	July-Sept	Oct-Dec	Year Total
%	40	20	10	30	100%

II. Process. Describe the process used to manufacture the subject chemical by providing the following:

1. Process name. If the process has a common name or description, give this. If any portion of the process (e.g., product recovery method) has a common name, give this.

2. Block Diagram. Provide a block diagram of the process showing the major process steps and stream flows.

   (a) Show on block diagram all streams described below. Identify each required stream by letter. (A,B,C, etc.) In general the streams that must be identified are (1) the gaseous emissions streams before and after any control device and (2) the gaseous or liquid streams which, after leaving the process site, produce gaseous emissions during further processing or combustion.

   (i) Any gaseous waste streams before and after any pollution device should be shown and identified.

   (ii) Streams from rupture disks or pressure relief valves which protect equipment from operating upsets but discharges less than once every year need not be shown.

   (iii) Emissions from pressure relief systems that normally discharge during power failures or other emergencies should be shown, identified by letter and labeled "emergency".

(iv) Emissions from fueled heaters such as "heat transfer medium" heaters, steam generators, or cracking furnaces need not be shown if they are fueled completely by fuels listed in Question VII and are not used to incinerate by-products or off gases.

(v) Emissions from Claus units associated with process need not be shown. Stream to Claus unit should be shown and identified with letter.

(vi) Emissions from a central power plant (or steam plant) which burns a liquid fuel produced as a by-product of this process need not be shown. Such liquid fuel should be shown and identified by letter.

(vii) Emissions from a central power plant (or steam plant) which burns a gaseous fuel produced as a by-product of this process need not be shown. Such gaseous fuel should be shown and identified by letter.

(b) Show all gaseous emission control devices. Identify each control device on the block diagram by a three digit number (101, 102, 103, etc.)

(c) Show all stacks or vents that vent streams listed in (a) and (b) above. It a stack to vent discharges emissions from more than one source, label this stack or vent with a letter in sequence started in II.2.a. (D,E,F, etc.) If a stack or vent discharges emissions from only one source label the stack with the same letter as the emission stream.

3. Raw material and product. Give approximate chemical composition and approximate amount (on yearly basis and at capacity given in I.1) of all raw-materials, products and by-products. If composition or amounts vary, give ranges. Composition may be given in commonly accepted terms when a chemical analysis would be inappropriate. The description "light straight-run naphtha" would be adequate.

4. Waste water. Is there a waste water discharge from this process which is (eventually) discharged to a receiving body of water? Is this waste water treated by you or by others? Give the approximate volume and indicate whether this is measured or estimated.

5. Waste solids. Is there a waste solids discharge from this process? How is it disposed of? Give the approximate daily total of waste solids and indicate if this is measured or estimated.

III. Emissions (composition and flow): For each stream requested in II.2.a. and shown on the block diagram by letter provide the following: (Use separate sheets for each identified location - 6 copies are provided). All of the questions will not be applicable for each stream.

As an example, question 10, odor problem, applies only to streams which are emitted to the atmosphere.

1. Chemical composition and flow. Give composition as completely as possible from information you have available. Do not omit trace constituents if they are known. If anything (e.g. fuel) is added upstream of any emission control devices, give the chemical composition and flow prior to the addition, and give the quantity and composition of the added material. If liquids or solids are present (in gas stream) provide the composition and amount of these also. Give flow volume (SCFM), temperature (F°) and pressure (psig or inches H_2O).

2. Variation in chemical composition and flow. If average stream composition or flow varies significantly over some period of time during normal or abnormal operation, discuss this variation and its frequency. Relate this to the average and range of composition given in III.1.

   As examples:

   "During start-up (once a month) the benzene is about 12% by volume for one hour" or "the benzene can be expected to go from 5% to 9% by volume during life of catalyst, the 'average' figure given is about average over the catalyst life" or "power failures occur about once each winter causing stream A to increase from 0 to (initially) 50,000 lbs/hr., and about 8,000 lbs is vented over a 15 minute period."

3. Production rate during sampling. If stream composition and volume flow rates given in answer to questions III.1. and III.2. were measured at a plant production rate different than the capacity of the plant given in I.1. give the rate at which the measurements were made.

   As example:

   Figures given for this stream (A) were made when plant was operating at 90% of capacity given in I.1.

4. Methods used to determine composition and flow. Is information from material balance, from sample and analysis, or other? Describe briefly.

5. Sampling procedure. If samples have been taken, give summary description of sampling procedure or give reference if described in open literature.

6. Analytical procedure. If samples have been taken, give summary description of analytical procedure or give reference if described in open literature.

7. Sampling frequency. How often is the stream sampled?

   As Examples:

   "continuous monitor" or "twice a shift for last 18 months" or "once in the fall of 1943".

8. Confidence level. Give some idea how confident you are in regard to compositions in III.1.

   As examples:

   "probably correct ± 20%" or "slightly better than wild guess".

9. Ease of sampling. How difficult is it to sample this stream?

   As examples:

   "sample line runs into control room" or "sample port provided but accessible only with 20-ft. ladder."

10. Odor problem. Is the odor of this emission detectable at ground level on the plant property or off the plant property? If odors carry beyond the plant property are they detectable frequently or infrequently? Have you received a community odor complaint traceable to this source in the past year? Has the odorous material been chemically identified? What is it?

IV. Emission control device. Supply the following information for each control device shown on the block diagram. (Use separate sheets for each - 3 copies are provided).

1. Engineering description. Give brief description and process sketch of the control device. Attach print or other description if you prefer. Show utilities used, steam produced, product recovered, etc. Give manufacturer, model number and size (if applicable). Give complete (applicable) operating conditions, i.e. flows, temperatures, pressure drops, etc.

2. Capital cost of emission control system.

   (a) Give capital cost for the emission control device as it is described in IV.1. above; i.e., if equipment has been modified or rebuilt give your best estimate of capital cost of equipment now in service. For the total installed cost give the approximate breakdown by year in which cost was incurred.

   As example:

   Major equipment cost $155,000
   Total installed cost $250,000

Year	Cost
1963	$160,000
1964	40,000
1971	50,000
	$250,000

   (b) On the check list given mark whether the items listed are included in total cost as given above. Give one sentence explanation when required but do not give dollar amounts.

   (c) Was outside engineering contractor used and was cost included in capital cost?

   (d) Was in-house engineering used and was cost included in capital cost?

   (e) Was emission control equipment installed when plant was built?

3. Operating cost of emission control system. Give the best estimate of cost of operating emission control system in dollars per year with process operated at capacity given in I.1. Other disposal (g) would include, as example, the cost of incinerating a by-product stream which has no value.

V. Stack or vent description. Each stack or vent should have been identified by letter on the block diagram. Provide the requested information for each stack. Stack flow, V.4. should be entered only when it is not possible to calculate this number by adding gas flows given in III.1.

An example would be when an off gas from the process is discharged into a power plant stack.

VI. Tankage. Give information requested for all tankage larger than 20,000 gallons associated with the process and normally held at atmospheric pressure (include raw material, process, product and by-product tankage). Method of vapor conservation (3.) might include, as examples:

"none, tank vents to air"
"floating roof"
"vapor recovery by compression and absorption".

VII. Fuels. If fuels are used in the process give the amount used on a yearly basis at capacity given in I.1. Do not include fuel used in steam power plants. Give sulfur content. Identify each fuel as to its source (natural gas pipeline, process waste stream, Pennsylvania soft coal). Is the fuel used only as a heat source (as with in-line burner)?

VIII. Other emissions. If there is a loss of a volatile material from the plants through system leaks, valve stems, safety valves, pump seals, line blowing, etc., this loss is an emission. In a large complex high pressure process this loss may be several percent of the product. Has this loss been determined by material balance or other method? What is it? Give best estimate.

IX. Future plans. Describe, in a paragraph, your program for the future installation of air pollution control equipment for this unit or for future improvements in the process which will reduce emissions.

OMB Approval Number 158 S 72019

This example questionnaire has been completed for a fictitious company and process.

Example Questionnaire

Air Pollution Control Engineering and Cost Study of the Petrochemical Industry

Please read instructions before completing questionnaire.

Subject chemical: Pyrrole

Principal by-products: Pyrrolidone

Parent corporation name: Orivne Petrochemical Co.

Subsidiary name: Noissime Division

Mailing address: P.O. Box 1234
Rianaelc, North Carolina, 27700

Plant name: Rianaelc Plant

Physical location: 30 miles N.W. Durham, North Carolina

(include county and air quaility control region) Orange County; Eastern Piedmont Intrastate (Region IV)

Person EPA should contact regarding information supplied in this questionnaire

Name: John Doe

Title: Supervisor of Process Development

Mailing address: Noissime Division of O.P.C.
P.O. Box 1234
Rianaelc, North Carolina, 27700

Telephone number: 919 XXX XXXX

Date questionnaire completed: May 30, 1972

I. Capacity.

1. Process capacity. (not production)

80,000,000 lbs. per year

10,000 lbs. per hour

2. Seasonal variation. (of production)

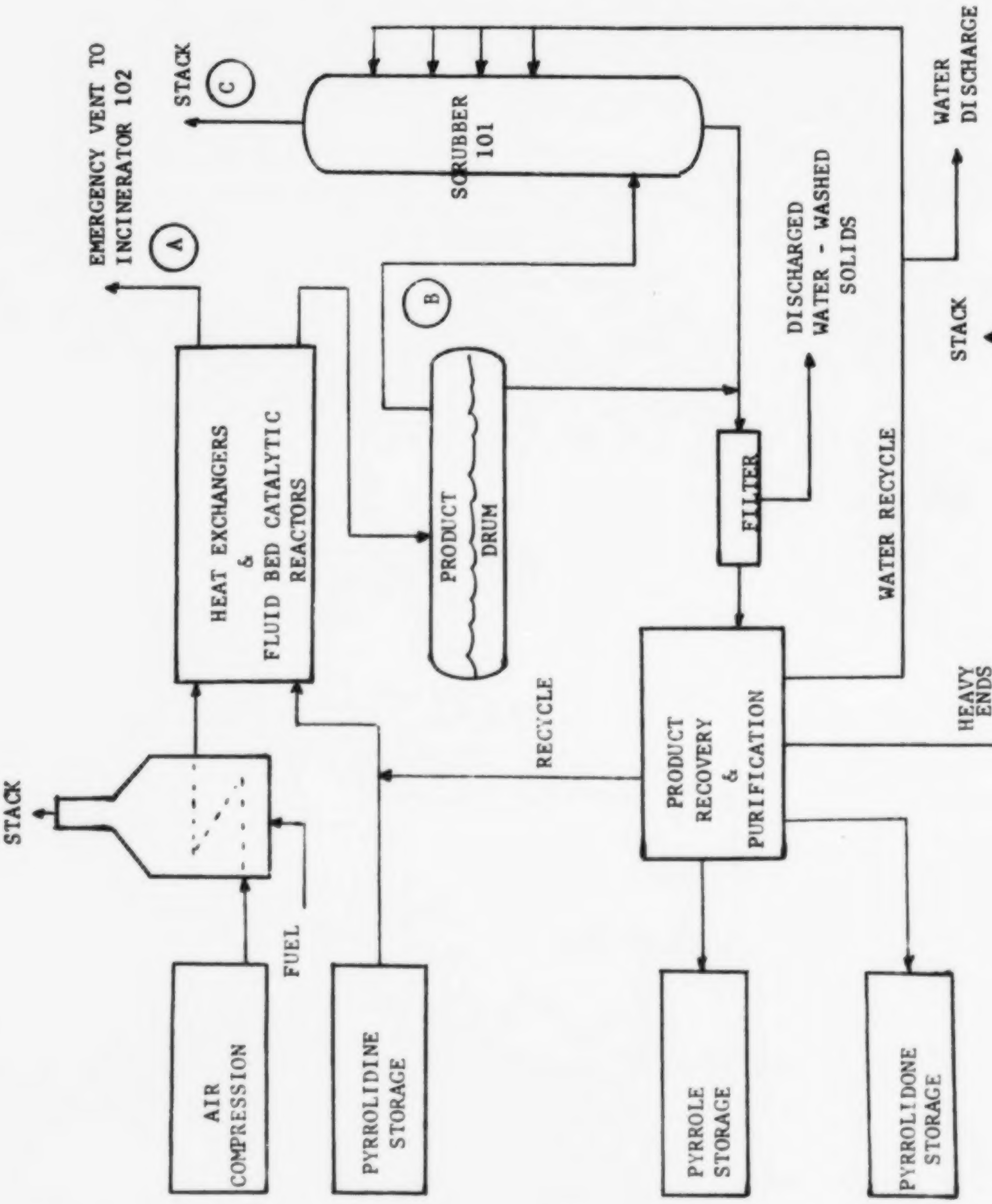
quarter	1	2	3	4	year total
%	30	20	20	30	100%

II. **Process.**

1. **Process name.**

Reivrep - Process (oxidative dehydrogenation of pyrrolidine)

2. **Block diagram.**


EMERGENCY VENT TO INCINERATOR 102
A
STACK
C
SCRUBBER 101
WATER DISCHARGE
B
DISCHARGED WATER - WASHED SOLIDS
STACK
E
HEAT EXCHANGERS & FLUID BED CATALYTIC REACTORS
PRODUCT DRUM
FILTER
WATER RECYCLE
INCINERATOR 102
RECYCLE
PRODUCT RECOVERY & PURIFICATION
HEAVY ENDS
D
STACK
FUEL
AIR COMPRESSION
PYRROLIDINE STORAGE
PYRROLE STORAGE
PYRROLIDONE STORAGE

II. Process. (Continued)

3. Raw materials and products

Raw materials

Name	Quantity	Composition
Pyrrolidine	130,000,000 lbs/yr.	pyrrolidine 98%
		other amines 2%

Product and by-products

Name	Quantity	Composition
Pyrrole	80,000,000 lbs/yr.	pyrrole 99.5%
Pyrrolidone	20,000,000 lbs/yr.	pyrrolidone 99.5%

II. Process. (Continued)

4. Waste water.

750 gal/hr. treated by us, measured in treatment unit.

5. Waste solids.

200 lbs/hr. catalyst dust from filter. Estimated average quantity hauled away by solids waste disposal contractor.

III. 1. Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter ___A___.

1. Flow ___?___ Temperature ___?___ Pressure ______.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid		

Depending upon cause of emergency, emissions could range from contaminated feed to contaminated product. Upset durations seldom exceed 15 minutes during which time incinerator operation would be modified. For initial 1-2 minutes after upset pollutants might leave incinerator stack. Following that, stack gases will be nearly 100% CO_2, H_2O & N_2. On average, such upsets occur two or three times per year. Particulates are possible, depending upon cause of upset. One such upset occurred in 1969.

* Particulate matter should be described as fully as possible.____________________

III. Continued For stream flow shown on block diagram by letter ____A____.

2. Composition variation.

   See III-1

3. Production rate during sampling.

   Never Sampled

4. Method used to determine composition and flow.

   Not applicable

III. Continued For stream flow shown on block diagram by letter A .

2. Composition variation.

See III-1

3. Production rate during sampling.

Never Sampled

4. Method used to determine composition and flow.

Not applicable

III. Continued For stream flow shown on block diagram by letter A .

5. Sampling procedure.

Not Applicable

6. Analytical procedure.

Not Applicable

7. Sampling frequency.

Never

III. Continued For stream flow shown on block diagram by letter A.

8. Confidence level.

Not Applicable

9. Ease of sampling.

Impossible

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?________________________________

Not Applicable

III.1. Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter B.

1. Flow 10,000 SCFM Temperature 110°F Pressure 25 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	150 lbs./hour	100-200 lbs./hour
Nitrogen	N_2	Gas	83.8 Vol. %	80-85%
Oxygen	O_2	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO_2	Gas	1.4 "	1-2%
Hydrogen	H_2	Gas	2.1 "	2-2.5%
Water	H_2O	Vapor	7.1 "	6.5-7.5%
Various Amines	**	Vapor	0.1 "	0.05-0.2%
Nitrogen Oxides	NO_x	Gas	300 VPPM	200-500 VPPM

* Particulate matter should be described as fully as possible. Catalyst Dust (composition is proprietary) contains cobalt and chromium on alumina base. 100% less than 15 microns; 60% less than 10 microns; 20% less than 5 microns; 5% less than 1 micron.

** Composition unknown - mixture of feed, products and other amines.

III. Continued For stream flow shown on block diagram by letter B .

2. Composition variation.

During 2nd and 3rd quarter when plant is operated below capacity, nitrogen is at high end of range and all other materials near low end. During start-up or plant upset (average about 50 hours/year) nitrogen is near low end of range and all other materials near high end.

3. Production rate during sampling.

Average composition based on rated capacity.

4. Method used to determine composition and flow.

Engineering calculation and plant material balance (flow). Composition calculated on basis of stream "C" analysis and estimated amine losses prior to installation of scrubber.

III. Continued For stream flow shown on block diagram by letter ___B___.

5. Sampling procedure.

Never sampled.

6. Analytical procedure.

Never Analyzed.

7. Sampling frequency.

See (5) above.

III. Continued For stream flow shown on block diagram by letter B.

8. Confidence level.

± 10%

9. Ease of sampling.

No sample taps are available, but one could be easily installed in readily accessible location. However, it would not be 8 pipe diameters from a disturbance.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?____________________

No applicable - this stream is no longer
emitted to the atmosphere.

III. 1. Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter C.

1. Flow 10,000SCFM Temperature 100°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	10 lbs./hour	5-20 lbs./hour
Nitrogen	N_2	Gas	83.9 Vol. %	80-85%
Oxygen	O_2	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO_2	Gas	1.4 "	1-2%
Hydrogen	H_2	Gas	2.1 "	2-2.5%
Water	H_2O	Vapor	7.1 "	6.5-7.5%
Various Amine	**	Vapor	50 YPPMV	30-100 PPMV
Nitrogen Oxides	NO_x	Gas	300 YPPMV	200-500 PPMV

* Particulate matter should be described as fully as possible. See "B". Size distribution 100% less than 5 microns; 60% less than 1 micron.

** See "B".

III. Continued For stream flow shown on block diagram by letter C.

2. Composition variation.

See "B"

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

See "B" for flow. Specific analysis methods are given in III-6(C)

III. Continued For stream flow shown on block diagram by letter C.

5. Sampling procedure.

   a. Particulates and moisture collected in sampling train as detailed in Federal Register, Dec. 23, 1971 (Method 5).

   b. NO_x sampled by EPA Method 7.

   c. Other constituents collected using grab sampling procedures for collection of gas. Sample size 10 liters in stainless steel tank.

6. Analytical procedure.

   a. Particulates and moisture determined gravimetrically as detailed in Federal Register, Dec. 23, 1971. (Method 5)

   b. NO_x determined by EPA method 7.

   c. Hydrogen, oxygen, and nitrogen determined by mass spectrometer analysis at local university.

      Amine, CO and CO_2 determined by infra-red analysis.

7. Sampling frequency.

   Once, - one month after scrubber was put on stream.

III. Continued For stream flow shown on block diagram by letter C.

8. Confidence level.

Oxygen, CO_2, CO and H may be ± 10%.

Nitrogen would be better than this, perhaps ± 5%

Amines are near limit of detection - ± 50%.

9. Ease of sampling.

Difficult - only sample tap is six feet above top of scrubber tower - approximately 65 feet in air - reached by caged ladders.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? [✓ Yes]/no Off the plant property? [✓ Yes]/no If odors carry beyond the plant property are they detectable infrequently? [✓ Yes]/no Frequently? Yes/[✓ no] Have you received a community odor complaint traceable to this source in the past year? Yes/[✓ no] Has the odorous material been chemically identified? [✓ Yes]/no What is it? Amine compounds.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter D .

1. Flow 300 GPH Temperature 300°F Pressure 10 PSIG .

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Heavy Amines	$(CH_x)_yNH_z$	Liquid	100%	

* Particulate matter should be described as fully as possible. Very fine catalyst dust - never sampled or analyzed - estimated to be 1-5 lbs./hour.

III. Continued For stream flow shown on block diagram by letter D.

2. Composition variation.

Not applicable - unknown - never analyzed.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Rotameter in liquid line for flow. Composition unknown.

III. Continued For stream flow shown on block diagram by letter D .

5. Sampling procedure.

Not applicable.

6. Analytical procedure.

Not applicable.

7. Sampling frequency.

Not applicable.

III. Continued For stream flow shown on block diagram by letter D.

5. Sampling procedure.

Not applicable.

6. Analytical procedure.

Not applicable.

7. Sampling frequency.

Not applicable.

III. Continued For stream flow shown on block diagram by letter D.

8. Confidence level.

Not applicable.

9. Ease of sampling.

Liquid drain line is available at ground level. Could be used for sample tap.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?____________________

Not applicable - not an emitted stream.

III. 1 Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter E.

1. Flow 10,000SCFM Temperature 450°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Nitrogen	N_2	Gas	77.0 Vol. %	76.5-77.5%
Oxygen	O_2	Gas	9.2 Vol. %	9-9.5%
Carbon Dioxide	CO_2	Gas	6.4 Vol. %	6-7%
Water	H_2O	Vapor	7.4 Vol. %	7-8%
Nitrogen Oxides	NO_x	Gas	150 VPPM	100-300 VPPM

* Particulate matter should be described as fully as possible. See "D"

III. Continued For stream flow shown on block diagram by letter E.

2. Composition variation.

Random variation depending on many variables such as production rate, ambient air temperature and humidity, catalyst age, etc., all within limits shown.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Calculation based on incinerator vendor's specifications, guarantees and laboratory tests.

III. Continued For stream flow shown on block diagram by letter E.

5. Sampling procedure.

Never sampled.

6. Analytical procedure.

Never analyzed

7. Sampling frequency.

See (5) above

III. Continued For stream flow shown on block diagram by letter E .

8. Confidence level.

± 10%

9. Ease of sampling.

No sample tap, very hot stream, no access ladders, minimal insulation.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/[✓ no] Off the plant property? [✓ Yes]/no If odors carry beyond the plant property are they detectable infrequently?* [✓ Yes]/no Frequently? Yes/[✓ no] Have you received a community odor complaint traceable to this source in the past year? Yes/[✓ no] Has the odorous material been chemically identified? [✓ Yes]/no What is it? Amines

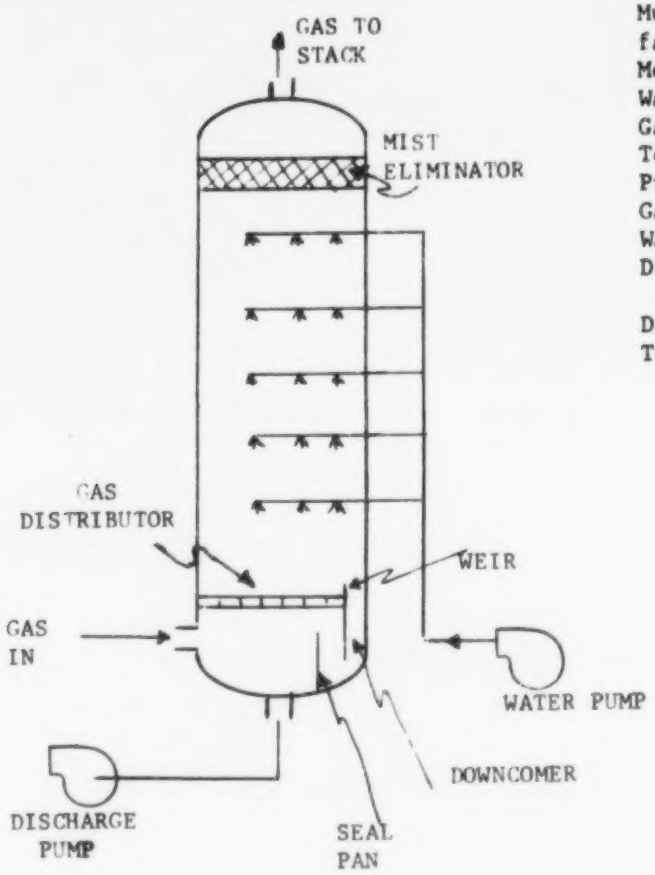
* Only during start-up or upset of the incinerator and then only if atmospheric conditions are favorable for ground level detection.

3 copies provided
this section.

IV. Emission control device

For device shown on block diagram by number 101.

1. Engineering description.


GAS TO STACK
MIST ELIMINATOR
GAS DISTRIBUTOR
WEIR
GAS IN
WATER PUMP
DOWNCOMER
DISCHARGE PUMP
SEAL PAN

Multi-nozzle spray tower manufactured by Rebburcs Corp.
Model No. 10,000-W
Water rate: 100 GPM
Gas rate: 10,000 SCFM
Temperature: 100°F.
Pressure: Atmospheric
Gas AP: 8 in, H_2O
Water Pump Head: 150 Ft.
Discharge Pump Head: 100 Ft.

Diameter of Tower: 6 Ft.
T-T Length: 60 Ft.

Utilities:

35 HP for Pumps

10,000,000 BTU/Hr. Additional steam in product recovery section.

1500 GPM Additional cooling water circulation in product recovery section.

IV. Continued For device shown on block diagram by number 101.

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost $ 160,000

Total installed cost $ 350,000

Year	Cost
1968	$350,000

IV. Continued For device shown on block diagram by number 101 .

(b) Check list. Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Additional foundation required for scrubber.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Rigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
	X	Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 101.

Yes	No	
X		Was outside engineering contractor used?
X		Was cost included in capital cost?
X		Was in-house engineering used?
	X	Was cost included in capital cost?
	X	Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a)	Utilities	$ 68,000
(b)	Chemicals *	10,000
(c)	Labor (No Additional Operators)	-
(d)	Maintenance (labor & materials)	14,000
(e)	Water treatment (cost of treating any waste water produced by this control system) **	-
(f)	Solids remmoval (cost of removing any waste solids produced by this control system)	20,000
(g)	Other disposal	-
(h)	By-product or product recovery CREDIT	($89,000)
	Total operating costs	$ 23,000

* Additional cooling water treatment included in utility costs - this cost is for corrosion inhibition in scrubber.

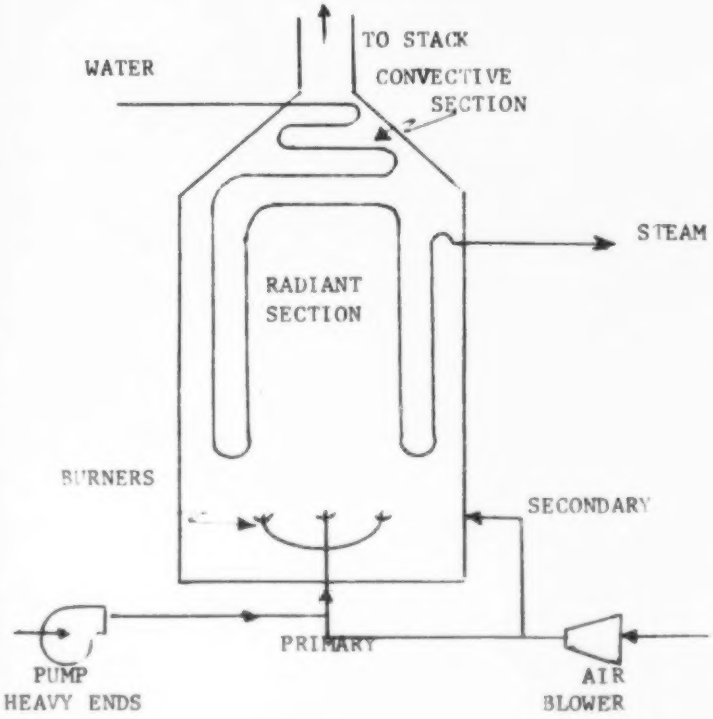
** Water waste is produced by process. It is treated at cost of $30,000/year. This treatment was required before scrubber was installed.

3 copies provided
this section.

IV. Emission control device

For device shown on block diagram by number 102 .

1. Engineering description.


TO STACK
WATER
CONVECTIVE SECTION
STEAM
RADIANT SECTION
BURNERS
SECONDARY
PRIMARY
PUMP
HEAVY ENDS
AIR BLOWER

Steam Generator/Waste Incinerator

Manufactured by: Xoberif Corp.
Model No.: 40-H
Heavy Ends Rate: 300 GPH
Air Rate: 9,500 SCFM
Steam Rate: 20,000 lbs./hour
Vessel Diameter: 15 Ft.
Height: 40 Ft.
Tube Diameter: 3 in. nominal
Tube Length: (Material)
  Convective (mild steel): 6,000 Ft.
  Radiant (304 stainless): 2,000 Ft.

Utilities:

Heavy Ends Pump: 20 HP

Blower: 100 HP

IV. Continued For device shown on block diagram by number 102.

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost $ 350,000

Total installed cost $ 1,000,000

Year	Cost
1960	$1,000,000

IV. **Continued** For device shown on block diagram by number 102.

(b) **Check list.** Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Cost prorated from total plant site costs.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Rigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
X		Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres, drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 102.

Yes	No	
X		Was outside engineering contractor used?
X		Was cost included in capital cost?
	X	Was in-house engineering used?
X		Was cost included in capital cost?
X		Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a)	Utilities	$ 5,000
(b)	Chemicals	-
(c)	Labor (½ man per shift - excludes supervision & overhead)	7,000
(d)	Maintenance (labor & materials)	40,000
(e)	Water treatment (cost of treating any waste water produced by this control system)	-
(f)	Solids remmoval (cost of removing any waste solids produced by this control system)	-
(g)	Other disposal	-
(h)	By-product or product recovery CREDIT- STEAM	($100,000)
	Total operating **credit**	$ 48,000

V. Stack or vent description.

For stack or vent shown on block diagram by letter C.

1. Stack height 100 ft
2. Stack diameter 2 ft
3. Gas temperature stack exit 100 °F
4. Stack flow * ________ SCFM(70°F & 1 Atm.)

For stack or vent shown on block diagram by letter E.

1. Stack height 60 Ft.
2. Stack diameter 3 Ft.
3. Gas temperature stack exit 450°F
4. Stack flow * ________

For stack or vent shown on block diagram by letter ________.

1. Stack height ________
2. Stack diameter ________
3. Gas temperature stack exit ________
4. Stack flow * ________

For stack or vent shown on block diagram by letter ________.

1. Stack height ________
2. Stack diameter ________
3. Gas temperature stack exit ________
4. Stack flow * ________

* See instructions

VI. Tankage.

No. of tanks	composition	temp.	capacity (each)	approximate turnovers per year	method of vapor conservation
3	Pyrrolidine $(CH_2)_4NH$	Ambient	100,000 gal.(ea)	50	None, vents to air
4	Pyrrole $(CH)_4NH$	Ambient	100,000 gal.(ea)	25	"
1	Pyrrolidone $(CH)_2CH_2CONH$	Ambient	100,000 gal.(ea)	25	"

VII. Fuels.

800,000 gal./year fuel oil for fired air heater 3% sulfur.

VIII. Other emissions.

No other known emissions although minor leakages probably occur.

Engineering estimate of average losses is 0.01% of throughput or 13,000 lbs./year of amines.

IX. Future plans.

1. Current research on heavy amine stream indicates further processing will produce a marketable product - if so, incinerator will be shut down.
2. We are currently negotiating a long term contract to purchase 1% sulfur fuel oil from the Flused Oil Company.

APPENDIX III

FINAL QUESTIONNAIRE SUMMARY

Chemical	Number of Questionnaires used as Basis for Report
Acetaldehyde via Ethylene	1
via Ethanol	1
Acetic Acid via Methanol	2
via Butane	1
via Acetaldehyde	1
Acetic Anhydride	2
Acrylonitrile	4
Adipic Acid	4
Adiponitrile via Butadiene	1
via Adipic Acid	2
Carbon Black	7
Carbon Disulfide	4
Cyclohexanone	7
Dimethyl Terephthalate (+TPA)	6
Ethylene	13
Ethylene Dichloride via Oxychlorination	10
via Direct Chlorination	3
Ethylene Oxide	7
Formaldehyde via Silver Catalyst	12
via Iron Oxide Catalyst	6
Glycerol	2
Hydrogen Cyanide	1
Isocyanates	10
Maleic Anhydride	7
Nylon 6	4
Nylon 6,6	3
Oxo Process	6
Phenol	8
Phthalic Anhydride via o-xylene	5
via naphthalene	3
Polyethylene (High Density)	5
Polyethylene (Low Density)	7
Polypropylene	7
Polystyrene	4
Polyvinyl Chloride	8
Styrene	7
Styrene - Butadiene Rubber	6
Vinyl Acetate via Acetylene	3
via Ethylene	1
Vinyl Chloride	8

INTRODUCTION TO APPENDIX IV AND V

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix IV discussion are:

1. Prediction of numbers of new plants.
2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix V discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX IV

Number of New Plants by 1980

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It is felt that no useful end is served by creating a large number of sub-groupings because it will merely compound the problem of assigning a weighting factor. Therefore, it is proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it is proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical____________________

Process____________________

Increased Capacity____________________

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	

Total____________________

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane will be included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. This determination is to be made on the basis of data reported on returned questionnaires.

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It is proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix V
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it is proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It is recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it is recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it is recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\,O_2 \longrightarrow C + 2\,CO + 3\,CO_2 + 6\,H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in Actual	Pounds in Weighted	Pounds out Actual	Pounds out Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0	____	66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ \text{(atmospheric)} + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

$$\text{However, } SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$$

$$\text{and } SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it is suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 95\%$$

$$\text{and SERR} = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\text{and SERR} = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$